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THE X-RAY CRYSTAL STRUCTURE OF SODIUM BROMIDE DIHYDRATE

William Robert Haaf
Metcalf Research Laboratory, Brown University,
Providence 12, Rhode Island

A Thesis submitted in partial fulfillment of the requirement for the degree of Master of Science in the Department of Chemistry at Brown University

June, 1963

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This thesis by William Robert Haaf
is accepted in its present form by the Department of
Chemistry as satisfying the thesis requirement
for the degree of Master of Science.

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I. The Aim of This Research

A great deal of the existent knowledge of the hydrogen bond in the solid state has been derived from X-ray crystallographic studies. The solution of the X-ray crystal structure of sodium bromide dihydrate will add to this basic information concerning the hydrogen bond.

It is of interest, at this point, to briefly summarize the work which eventually led to this thesis investigation.

It has been reported (Mutter, Mecke and Lüttke, 1959) that a hitherto unknown form of ice resulted when water vapor was slowly condensed onto a sodium chloride plate kept at a low temperature. The infrared spectrum of this substance showed sharp lines, in marked contrast to the spectra of cubic and of hexagonal ice. A repetition and extension of this work at Princeton University (Hornig and Schiffer, 1961) indicated that the proposed new form of ice is, in reality, the dihydrate of sodium chloride. Comparison of the infrared spectrum of sodium chloride dihydrate with that of sodium bromide dihydrate, produced by condensation of water vapor upon a sodium bromide plate, suggested that the two structures are very similar. Schiffer and Hornig also studied these salt hydrates, again by infrared methods, after having introduced small replacements of HDO for the H_2O or D_2O present in the hydrates. They concluded that there is some evidence of O-H····X^- and O-H····O bonding. The problem of whether or not all the hydrogen atoms are involved in hydrogen bonding was called to our attention by

Hornig's private communication, during the summer of 1961, to G. B. Carpenter.

By examination of the interatomic distances in the sodium bromide dihydrate crystal, it should be possible to confirm and extend the findings of Schiffer and Hornig. It was also desired to investigate the possibility that, from a well-refined crystal structure model of this hydrate, the hydrogen atoms may be evident in a three dimensional difference electron density synthesis.

During the final stages of this investigation, it was learned that Van Meerssche, Culot and Piret (1962) had recently completed their independent determination of the crystal structure of sodium bromide dihydrate by X-ray methods. The reported details of the structure are essentially the same as those concluded in this work. More detailed comparisons will appear later.

II. Experimental Procedures

A. Preparation of Sodium Bromide Dihydrate

The method of preparation of sodium bromide dihydrate (Gmelin, 1928, p. 420-421) is simply recrystallization from an aqueous solution of sodium bromide.

A water solution of sodium bromide, saturated at 42°C, was prepared in a beaker which was kept in a thermostatted electric oven. By controlled, very slow cooling of the oven down to room temperature (about 25°C), large, irregular, flat plates of translucent material arranged in step-wise layers crystallized out of the solution. These plates could be easily broken apart by mechanical means to yield what appeared to be single crystals. The percentage of water in the substance was determined roughly by weighing a sample before and after heating in an oven. It corresponded to the molecular formula $NaBr \cdot 2H_2O$.

B. Growth and Mounting of a Single Crystal.

There were three considerations involved in the problem of growing and using a single crystal of sodium bromide dihydrate in an X-ray study. Firstly, if a crystal of this substance were left exposed to the air, it would either deliquesce or effloresce strongly, depending upon the prevailing atmospheric conditions. Secondly, the "optimum" cross-sectional diameters (assuming a cylindrical crystal) are 0.142 mm for CuK_α radiation and 0.197 mm for MoK_α radiation. (These values were calculated from the equation $t = 2/\mu$ (Buerger, 1942), where μ is the linear absorption coefficient in cm^{-1} calculated from $\mu = d \sum_i p_i (\mu/\rho)_i$.

In the latter equation, d is the density of the crystal in $gm\text{-}cm^{-3}$, p_t is the weight-fraction of the ith element in the compound, and $(\mu/\rho)_t$ is the mass absorption coefficient in $gm^{-1}cm^2$, characteristic of the ith element and the type of X-radiation used.) Growing and handling of a very small "optimum-size" crystal would be somewhat awkward. Finally, if an irregularly-shaped crystal were used, the correction for its absorption of X-rays would be complicated.

These problems could be neatly solved by growing single crystals, again from saturated solutions as outlined above, in 5-8 cm lengths of thin-walled Pyrex capillary tubing of inside diameter about 0.1-0.2 mm. After warm, saturated solution was drawn up into the capillaries, both ends were sealed off with Picein wax. A large number of these capillaries containing crystalline material were examined, both visually and under a polarizing microscope, in order to detect possibly serious defects of shape, size, or possible twinning in the crystals. Finally, a practically cylindrical crystal measuring about 0.19 mm. in diameter and 3 mm in length, contained in a 5 cm length of capillary, was deemed acceptable for the subsequent X-ray photography. The capillary was carefully snapped off and re-sealed with Picein wax so as to leave a 3 cm length of capillary, with the desired crystal about 1 cm from one end. The other end was mounted by means of Picein wax on the end of an 8 mm. length of solid glass rod 3 mm in diameter. This rod was then inserted in the opening provided on a goniometer head. The crystal could then be placed in the path of the X-ray

beam by screwing the whole goniometer head into place on the chosen X-ray diffraction camera.

C. Recording of X-Ray Diffraction Spectra

1. Apparatus and Equipment Involved

a. X-Ray Sources

The X-rays were produced from sealed, water-cooled X-ray tubes set in a Norelco X-ray Diffraction Unit of Type 12031, manufactured by the North American Philips Co., New York, N.Y. Tubes with targets of molybednum and of copper were used. Unfiltered molybdenum radiation was employed for all orientation photographs, but practically monochromatic radiation was desirable for other purposes. MoK_α radiation was partly isolated by intercepting the X-ray beam with a zirconium filter, CuK_α by interception with a nickel filter. The molybdenum radiation was produced at a filament current of 15-20 ma and voltage of 55 kV, the copper radiation at 20 ma and 35 kV. Molybdenum radiation was used for most intensity photographs to minimize absorption of the X-rays; copper radiation was used only to obtain certain small-angle reflections.

b. Cameras

Use was made of the Weissenberg camera and of the Buerger precession camera, both of which were manufactured by the Charles Supper Co., Newton Center, Mass. The Weissenberg camera accommodates an approximately 12½ by 14½ cm rectangle of X-ray film, whereas 12½ cm squares of X-ray film are usually fitted into the precession camera.

In practice, the film which is loaded into the

Weissenberg camera is translated back and forth as the crystal, bathed in the X-ray beam, is rotated. (In this case, the rotation axis was the long axis of the capillary containing the single crystal of sodium bromide dihydrate.) By use of a cylindrical metal screen called a layer-line screen, it is possible to limit the film-recorded reflections to those in a given plane of the reciprocal lattice. The resulting developed photograph shows "festoons" of spots which represent a distorted picture of a single plane of the reciprocal lattice. The distortion, however, does not prevent one from assigning hkl indices to each spot with relative ease. A comprehensive, detailed explanation of the principles and geometry of the Weissenberg camera, the recording of reflections by the equi-inclination method, and the simple technique for rapid indexing is presented by Buerger (1942, pp. 214-295).

The geometry of motion involved in the precession method of photography is somewhat complicated; the normal to the reciprocal lattice plane being photographed sweeps out a circular cone about the X-ray beam. The precession method has the advantage of providing undistorted pictures of the reciprocal lattice, thus facilitating the rapid and accurate determination of unit cell constants, as well as making the indexing quite obvious. A further advantage is seen in that it is possible to photograph several groups of planes while the crystal is mounted in a single orientation. There is, however, a blind spot present at the center of the diffraction pattern of each

level, and this blind spot increases rapidly in area as the distance from the reciprocal lattice origin increases. Full details of the precession method are presented in the Supper Co. Manual and in an ASXRED monograph (Buerger, 1944). Both Weissenberg and precession intensity photographs were taken in the course of this study.

c. Film, Developing Materials and Procedure

No-Screen Medical X-Ray Film, manufactured by Eastman Kodak Co., Rochester, N.Y., was used for all X-ray photographs. Black cellulose acetate plastic was used to shield the X-ray film from light and to hold the film in place in the camera.

The developing procedure for all photographs was as follows: The exposed film was immersed for 5½ minutes in Kodak X-Ray Developer treated with Kodak AntiFog No. 2 (0.3 g/l of developer), held in a dilute acetic acid "stop" bath for about 3 seconds, immersed in Kodak X-Ray Fixer for twenty minutes, and washed finally in cold running water for 30 minutes.

2. X-Ray Diffraction Photographs

a. Weissenberg Photographs

The crystal was oriented on the Weissenberg apparatus by making use of 20° oscillation photographs taken 90° apart. By adaptation of Bunn's method (1946, p.173-174), it was possible to estimate the correction to be applied to the crystal setting in order that the rotation axis and the c (crystallographic) axis should coincide. (The c axis was so designated to facilitate comparison between the cell

parameters obtained in this study and those obtained by Wooster (1932)). The orientation of the crystal was checked by examination of a 6-hour rotation photograph. Two series of 24-hour Weissenberg intensity photographs of the $\underline{a}^*$-$\underline{b}^*$ plane were made with an oscillation range of about 200°. The first series was made using MoK_α radiation; levels 0,1,2,3,4, and 5 were included in this series. The second series was made using CuK_α radiation; levels 0,1,2, and 3 were included in this series. These two sets of photographs complemented each other inasmuch as the MoK_α set provided good, large angle intensity data, while the CuK_α set provided small angle reflections not available on the MoK_α set. Both series employed the multiple film technique as described, for example, by Richards (1959). For MoK_α radiation, the pack of three films was separated by two thin sheets of brass foil before being loaded into the camera. But for both MoK_α and CuK_α radiation, the ratios of the intensities of a given diffraction spot recorded simultaneously on the three films was about 16:4:1. In this manner, most of the weakest and strongest intensities were conveniently measurable. All of the intensities belonging to one given reciprocal lattice level were subsequently placed upon the same numerical scale by the application of film scale factors.

b. Precession Photographs

The crystal was transferred to the precession apparatus for orientation. Since the crystal had already been oriented for Weissenberg photography, only the dial

axis of the precession instrument needed adjustment for the $\underline{a}^*$-$\underline{c}^*$ plane to be in photographic position. The amount of this adjustment could be found by examination of a zero-level Weissenberg exposure for the position of reflection of the spots aligned along the $\underline{b}^*$ axis. Final adjustments were carried out with the aid of the "Orientation Error Chart for Precession Method" (Supper Co. Manual). Measurements obtained from a cone-axis photograph, coupled with the application of a standard chart (Evans, Tilden and Adams, 1949), provided camera settings which led to the precession photography of five reciprocal lattice levels--levels 0,1,2,3 and 4. Exposures of 24 hours, 6 hours and 1½ hours were made of each level. It should be noted that about midway through the precession intensity series, a whitish cast had developed upon the surface of the crystal, indicating that some deterioration of the crystal had taken place during its exposure to X-rays. That the deterioration did not significantly affect the diffraction properties of the crystal was shown by the comparison of a first-level photograph taken before the whiteness was noticed with one taken well after it became visible.

D. Determination of Unit Cell Dimensions

1. Film Measurements

Preliminary examination of the Weissenberg and precession records showed that Wooster's (1932) monoclinic unit cell is correct. His choice of $\underline{b}$ as the unique axis was retained.

Measurements were performed on a zero-level

precession film in order to determine $\underline{a}^*$ $\underline{c}^*$ and cosine β^*. Another zero-level precession film, obtained after rotating the precession spindle axis 90°, was used to determine $\underline{b}^*$. Seventy-two spot positions and twelve spot positions, respectively, were measured to 0.01 mm with the aid of a film viewer manufactured by the Charles Supper Co., Newton Center, Mass.

2. Calculating the Cell Dimensions

The reciprocal cell parameters were calculated by application of the method of least squares, which, in this case, minimized the quantity $\sum \omega_{hkl}(S_o^2 - S_c^2)^2$. In this expression, S_o^2 is the observed squared reciprocal lattice vector calculated for reflection hkl by the quantity $4 \sin^2\theta/\lambda^2$, where θ is the Bragg angle for reflection hkl, and λ is the wavelength of X-radiation used in recording the reflection; w_{hkl} is the weight assigned to S_o^2. The sum is taken over all the measured reflections. Weights were subjectively assigned on the basis of the magnitude of $\underline{S}$ and ease of measurement of the spot position. It was a simple matter to convert the reciprocal cell constants into those of the direct lattice.

The standard deviations associated with $\underline{a}^*$, $\underline{c}^*$ and β^* were calculated by means of the equation for the variance, σ_i^2, which is $\sigma_i^2 = \left[\frac{1}{m-s}\frac{D_{ii}}{D}\right]\sum_{j=1}^{m}(S_{o_j}^2 - S_{c_j}^2)^2$ (Whittaker and Robinson, 1940), where m is the number of observational equations, s is the number of parameters involved, D_{ii} is the ith cofactor of the determinant D of the coefficients of the normal equations, and $(S_{o_j}^2 - S_{c_j}^2)^2$ is the

residual of the jth observational equation. The standard deviation of $\underline{b}^*$ was obtained in like manner. Again, the standard deviations in the direct cell constants may be easily obtained from these. It must be realized that the standard deviations in the cell constants are measures only of the internal consistency of the data, and do not take systematic errors into account. (The sources of such errors may be, for example, film shrinkage, or failure to calibrate the X-ray cameras. These factors were not corrected for in this work.)

3. Discussion of the Cell Dimensions

The only X-ray work on sodium bromide dihydrate published prior to the beginning of this study was a determination of the cell constants and space group by Wooster (1932). He employed Weissenberg and oscillation photographs for this purpose.

Very recently, Van Meersche, Culot, and Piret (1962) have also determined cell constants (in the course of their complete structure determination) by making use of Weissenberg and rotation photographs. For comparison, Table I below lists the cell parameters, number of molecules per unit cell, and the calculated densities resulting from the three independent investigations. Note that the limits given in this work are standard deviations. The actual errors are probably of the same order of magnitude as those of Van Meersche and co-workers.

Upon examination of Table I, it is clear that Wooster's set of cell constants do not approach the value "4" for the calculated number of molecules per unit cell quite as well as do the other two sets. Moreover, the agreement is quite good between the individual axial lengths and monoclinic angle given here and those given by Van Meerssche and co-workers. For these reasons, it would seem that either of these two sets of cell parameters are preferable to Wooster's.

TABLE I

Comparison of Unit Cell Quantities

Quantity	This Thesis Work (1963)	Van Meerssche and co-workers (1962)	Wooster (1932)
a	6.575±0.002Å	6.57±0.03Å	6.59Å(±0.5%)
b	10.456±0.005Å	10.38±0.05Å	10.20Å(±0.5%)
c	6.776±0.002Å	6.78±0.03Å	6.51Å(±0.5%)
β	113°23'±0.002°	113°30'±0.4°	112°5' (±0.5%)
Calc'd No. Molecules per Unit Cell	4.04	4.00	3.83
Calc'd Density	2.16 23-25°C room temp.	2.18 unspec'd room temp.	2.16 unspec'd room temp.

Experimental Density is D_4^{20} = 2.176±0.003 (Gmelin, 1928)

E. Determination of the Space Group

It was already indicated that the cell parameters of sodium bromide dihydrate are characteristic of the monoclinic crystal class. In addition, it was noted upon examination of the X-ray photographs that, for the class of h0l reflections, only those for which l=2n (n is an integer) were present, and that for the class of 0k0 reflections, only those for which k = 2n were present. It was then possible to determine the space group corresponding to these systematic absences as $P2_1/c$ uniquely (Internationale Tabellen, 1935, p. 382). This finding is in agreement with those of Wooster and of Van Meerssche.

F. Obtaining Structure Factor Magnitudes from Corrected Relative Intensity Data

1. Microphotometer Method for Measuring Intensities on Precession Films

All intensity measurements of diffraction spots on precession films were made with the aid of a Recording Microphotometer manufactured by the F. C. Henson Co., Pasadena, California. The original recording and detection system was modified to consist essentially of a light source and a photomultiplier tube electrically connected to a microammeter. The procedure of estimating an intensity was as follows: The spot, the intensity of which was desired, was positioned so that the area of the spot's maximum blackness intercepted a light beam which impinged upon a photoelectric cell. The amount of light which passed through the spot was indicated by the deflection of a sensitive microammeter.

The background (that is, the intensity of the area immediately surrounding a spot) was also measured in the same way. The relative intensity of the given spot is then I_{rel} = log (average galvanometer reading corresponding to background) - log(galvanometer reading corresponding to spot). In this study, the differences were multiplied by 100 for numerical convenience. It was necessary to measure only half of the reflections recorded on the intensity photograph; one half of a given film was related to the other half by a center of symmetry.

2. Visual Method for Measuring Intensities on Weissenberg Films

An adaptation of the visual method described, for example, by Lee (1958) was used in this study, since the arrangement and shape of the Weissenberg spots did not facilitate the measurement of their intensities by the microphotometer method. In addition, the opportunity of comparing the intensities resulting from the two different methods of measurement is presented.

The visual method consists in comparing the intensity of a given spot to the intensities of one or two spots belonging to a series of spots of assigned, graded, relative intensities. By interpolation, an estimated value of relative intensity is assigned to the given spot. In order to obtain the desired series of spots for purposes of comparison, it was necessary to prepare an "intensity strip". The intensity strip was made as follows:

A region of reflection within the crystal corresponding to a suitable diffraction spot on the film (suitable in blackness, absence of strong background, and shape) was isolated within a 4-8° oscillation on the Weissenberg apparatus. The reflection region was exposed to X-rays for a pre-determined length of time (or number of oscillations) causing the corresponding spot on the processed film to be blackened accordingly. The film was given a 3 mm translation, and the reflection region again exposed to X-rays for another known length of time. The process was repeated until a series of 20 spots, arranged in a straight line and graded in blackness, were produced. The time intervals of X-ray exposure followed a geometric series of form $(\text{base})^x$ = exposure time, where, in this study, the base is 1.25, x assumes all integral values from 0-19, and exposure time is in minutes. In principle, any numerical base with any regular sequence of exponents could be utilized, and the result could be expressed in any time units, depending upon the nature of the crystal used. A geometric series of exposure times was employed because the neuro-physiology of the eye is such that it responds to the logarithm of the exposure time rather than to the exposure time itself when estimating intensities. Thus, if a geometric series of time exposures is chosen, the eye sees the same interval of blackness between any two successive spots in the intensity strip.

Usually, when the relative intensity of a given spot was estimated, it was between two spots (in blackness)

on the intensity strip. To obtain the desired relative intensity, use was made of the relation $\log I_x = r \log I_d + (1-r) \log I_l$, where I_x is the desired relative intensity of the given spot, I_d is the relative intensity of the darker spot, I_l is the relative intensity of the lighter spot, and r is the fraction of interpolation. It was found convenient to construct a table of values of I_x for the r values of 1/5, 1/4, 1/3, 2/5, 1/2, 3/5, 2/3, 3/4 and 4/5. Thus, all that needed to be done, in practice, was to write down the exponent corresponding to the lighter reflection together with the fraction of interpolation, and I_x could then be easily read off from the table. The intensity of every spot that could be detected by eye on the Weissenberg films was visually estimated.

All Weissenberg and precession intensity measurements were performed in no particular order, and under conditions which were as uniform as possible. Film factors were computed after all intensity measurements were completed in order to eliminate bias.

3. Comparison of the Microphotometer and Visual Methods

The microphotometer method yields measurements of slightly greater precision than are obtained by the visual method. A microphotometer measurement may enjoy 5-10% reproducibility whereas a visual measurement ranges from 5-15% in reproducibility. Furthermore, the microphotometer method depends less upon the physical condition of the experimenter and less upon local lighting conditions.

On the other hand, it must be noted that the microphotometer method yields peak intensities rather than the more desirable integrated intensities given by the visual method. In addition, it cannot be denied that the visual method is faster, enabling one to perform 2 or 3 measurements in the same time required for one measurement by the microphotometer method. This fact is of some importance if one is interested in obtaining the intensities of a thousand or more diffraction spots. Finally, serious errors are more likely to be avoided if one is able to measure an hkl reflection several times by the visual method rather than once or twice by the slightly more precise microphotometer method.

Taking all factors into consideration, it is the author's opinion that, in spite of the slight superiority in precision of the microphotometer method, and that provided good intensity strips can be readily made, the visual method, which produces rapid estimates of integrated intensities, is generally the more desirable method.

4. Extraction of Structure Factor Magnitudes from Relative Intensities

Squared structure factor magnitudes were obtained by multiplying the relative intensities, the I_{hkl}'s, by the reciprocals of the Lorentz and the polarization factors. Mathematically, $|F_{hkl}|^2 = (Lp)^{-1}_{hkl} I_{hkl}$ (Buerger, 1960, pp. 25-48), where $|F_{hkl}|$ is the magnitude of the structure factor corresponding to reflection hkl, and $(Lp)^{-1}_{hkl}$ represents the reciprocal product of the Lorentz factor (including any geometrical factors associated with the

particular method of X-ray photography employed) and the polarization factor.

A set of Lorentz-polarization charts reproduced upon transparent film were available for use in applying the Lorentz-polarization correction to the relative intensity data obtained from precession films. Save for adjustments of scale, these charts are identical to those made by Waser (1951), and by Grenville-Wells and Abrahams (1952). Waser constructed a Lorentz-polarization chart for the zero level of the reciprocal lattice and precession angle $\mu = 30°$; the seven Grenville-Wells charts are constructed at intervals of 0.05 reciprocal lattice units above the zero level, again for $\mu = 30°$. Linear interpolation was applied to obtain Lorentz-polarization factors for precession films corresponding to intermediate reciprocal lattice levels. Extraction of the square roots of the squared structure factor magnitudes resulted in a set of "precession" structure factor magnitudes.

The Lorentz-polarization corrections for relative intensities from Weissenberg films were applied by computer means at the Brown University Computing Laboratory. A program developed for this purpose was utilized (Carpenter and Hall, 1962, pp. 8-12). A set of "Weissenberg" structure factor magnitudes along with their corresponding squared values were obtained as computer output.

5. <u>Placing All Structure Factor Magnitudes on the Same Scale</u>

In the preceding, it was explained how relative

structure factor magnitudes were obtained for reflections appearing on films corresponding to seven reciprocal lattice levels photographed by the Weissenberg method, and for reflections appearing on films corresponding to five reciprocal lattice levels photographed by the precession method.

The next problem was that the structure factor magnitudes corresponding to one film were on a numerical scale different from that for any other of the twelve films. It was necessary to place all the structure factor magnitudes on the same numerical scale by finding and applying twelve scale factors, k_1, k_2, k_3,.....k_{12}, to the structure factor magnitudes corresponding to the twelve films. Evaluation of these scale factors depended on the fact that a considerable number of reflections were recorded at two film positions, once on a precession film and again on a Weissenberg film.

In order to find the set of k's which would lead to the best adjustment of all the structure factor magnitudes, it was decided to apply a modification of the method of Rollett and Sparks (1960). The finding of the best set of k's became essentially a least-squares problem. The function which was minimized with respect to the k's is $E = \sum_{i,j} \sum_{\underline{S}ij} \omega(\underline{S}_{ij}) \left[k_i F_i(\underline{S}_{ij}) - k_j F_j(\underline{S}_{ij}) \right]^2$. Subscripts i and j refer to two different films of a total of N different films to be correlated; $\underline{S}ij$ designates reflections common to films i and j; $F_i(\underline{S}_{ij})$ is the magnitude of the structure factor for reflection $\underline{S}_{ij}$ as measured on film i; k_i is the scale factor to be applied to the structure

factor magnitudes of film i; $w(\underline{S}_{ij})$ is the weighting factor to be applied to reflection $\underline{S}_{ij}$. It was necessary to introduce an undetermined multiplier to find a set of k's other than $k_i = 0$ for all i. The problem then became one of solving a 12X12 matrix for the minimum eigenvalue and its associated eigenvector (or set of scale factors). Fortunately, the Brown Computing Laboratory facilities together with an eigenvalue-eigenvector program written by T. Hughes were available. Thus, after the proper matrix coefficients were set up with aid of a desk calculator, the eigenvalue and eigenvector were readily found.

After application of the scale factors to the films, it became evident that certain corrections should have been applied to the "raw" (that is, uncorrected for the Lorentz-polarization factors) intensity data of the precession films. Since only peak precession intensities had been measured by the microphotometer method, it was necessary to correct for the area of the spot. (The need for this correction, however, does not arise if one measures intensities by the visual method, owing to the eye's natural allowance for area.) The correction was carried out by the following semi-empirical means.

Assume a roughly conical distribution in the diffraction spot intensity. The microphotometer method yields a measure of the cone height, h, only. Now consider the integrated intensity of a diffraction spot to be roughly analogous to the volume of a cone. In other words, assume that the raw, integrated intensity, I, is given by the

product of the height, h, and base area, A, of the cone. But since A may be expressed empirically in terms of h by the relation $h = A^n$, $I_{raw} = hA = h^{(1+1/n)}$; hence n may be evaluated by a log h vs. log A plot. About 12-15 precession spots, varying in blackness, were chosen for the plot. The spot areas were measured with a travelling microscope. The log-log plot showed considerable scatter, but, nevertheless, it was possible to draw what appeared to be a reasonable straight line through the distribution of points. This line led to the expression for the corrected raw intensity $I_{raw}=h^{1.26}$, which was used to correct all the previously-measured precession intensities. A new set of structure factor magnitudes was derived from the corrected precession intensities. After the eigenvalue-eigenvector program was applied, using the corrected precession structure factor magnitudes, a set of k's resulted which led to reasonably well-correlated structure factor magnitudes. In this way, structure factor magnitudes, all on one numerical scale, were obtained for 634 independent reflections. At this point, it was possible to begin the detailed structure investigation of sodium bromide dihydrate.

III. Determining the Detailed Structure of Sodium Bromide Hydrate

A. The Phase Problem of X-Ray Crystallography

The structure factor, F_{hkl}, is, in general, a complex quantity which may be expressed as a product of $|F_{hkl}|$, the structure factor magnitude for reflection hkl, and $e^{i\phi_{hkl}}$, the phase factor. If the complex structure factor, F_{hkl}, were experimentally available, solving a crystal structure would be a routine matter. Knowledge of the F_{hkl}'s would enable one to evaluate the electron density $\rho(x,y,z)$, at any point x,y,z in the unit cell from the relation $\rho(x,y,z) = 1/V \sum \sum \sum F_{hkl} e^{-2\pi i(hx+ky+lz)}$ (Lipson and Cochran, 1953, p. 12), the summation extending over all indices hkl. An electron density map could then be constructed, which would reveal the atomic positions in the unit cell. But thus far, it has been possible to obtain only structure factor magnitudes by experimental means. It would seem that, owing to the lack of phase information, the solution of a crystal structure would be at least very difficult. This constitutes the phase problem of X-ray crystallography expressed, for example, by Buerger (1960, p. 551). One attack on the phase problem is by means of the Patterson (or $|F|^2$) synthesis.

B. The Patterson Synthesis

1. The Physical Significance of the Patterson Function

An insight into the physical significance of the Patterson function, P(u,v,w), is provided by examination of one expression of P(u,v,w) which is

$P(u,v,w) = V\int_0^1\int_0^1\int_0^1 \rho(x,y,z)\ \rho(x+u,y+v,z+w)dxdydz.$

This relationship expresses the fact that the Patterson function, evaluated for the chosen vectorial distance u,v,w, is given by the product of $\rho(x,y,z)$, the electron density at x,y,z and $\rho(x+u,y+v,z+w)$, the electron density at x+u,y+v,z+w. Fractional coordinates x,y,z may vary through all values from 0 to 1, while u,v,w are held fixed. The highest positive numerical value of the Patterson function will be at those particular values of u,v, and w which are coordinate differences between peaks in the electron density, or which, in other words, correspond to certain interatomic vectors. Whereas an interatomic vector may have its origin anywhere in the unit cell, that vector must begin at the origin in "Patterson (or vector) space". The preceding was condensed from Buerger's book (1959, chapter 2), which contains a detailed discussion of the theory and application of the Patterson function.

2. Forms of the Patterson Function Suitable for Calculation

The general expression for the Patterson function is given as (Lipson and Cochran, 1953, pp. 9-15)

$P(u,v,w) = 1/V\sum\sum\sum |F_{hkl}|^2\cos 2\pi(hu+kv+lw)$, where u,v,w refer to fractions of the lengths of a,b,c axes, respectively, V is the unit cell volume, and the triple summation is taken over indices h,k, and l. By taking advantage of the space group symmetry of the particular substance under study, the general expression is usually modified to facilitate practical calculation. The modifications involved in the

calculation of the Patterson projection and the three-dimensional Patterson synthesis, both for space group $P2_1/c$, will be considered next.

Before all the intensity data had been gathered, a zero-level Patterson projection was constructed, using the available squared structure factor magnitudes of the zero-level precession film, in order to obtain preliminary indications of the structure of sodium bromide dihydrate. Since a Fourier synthesis computer program had not been completed at that time, the Patterson projection was calculated with Beevers-Lipson strips (Lipson and Cochran, 1953, pp. 89-93). The general form of the Patterson function (as given above) had to be modified in the following manner to allow the efficient use of this strip method. Since the projection was along the b axis onto the zero level, k = 0, and the general form could be written as $P=1/A \sum_{-\infty}^{+\infty} \sum |F_{h0l}|^2 \cos 2\pi(hu+lw)$. (This form may be derived by observing that an electron density projected in a certain direction corresponds mathematically to an integration over the lattice period in that direction (Buerger, 1960, p. 382)). In this case, $\rho(x,z) = \int_0^1 \rho(x,y,z)\,bdy$, where b refers to the axis along which the projection is taken, $\rho(x,z)$ is the projected electron density at point x,z, and $\rho(x,y,z)$ is the electron density at x,y,z. The form of Patterson projection could then be obtained by a treatment similar to that given by Lipson and Cochran (1953, pp. 11-13).) Application of the trigonometric identity $\cos(\alpha + \beta) = \cos\alpha \cos\beta - \sin\alpha \sin\beta$ resulted in

the form

$$P=1/A\sum_{-\infty}^{\infty}\sum_{-\infty}^{\infty}|F_{h0l}|^2\left[\cos(2\pi hu)\cos(2\pi lw)-\sin(2\pi hu)\sin(2\pi lw)\right].$$

It was necessary to measure the intensities appearing on only one-half of the film (see section IIF 1), hence the summation could be split up to appear as $1/4P =$

$$1/A\sum_{0}^{\infty}\sum_{-\infty}^{\infty}|F_{h0l}|^2\left[\cos(2\pi hu)\cos(2\pi lw)-\sin(2\pi hu)\sin(2\pi lw)\right]+$$

$$1/A\sum_{0}^{\infty}\sum_{-\infty}^{\infty}|F_{\bar{h}0l}|^2\left[\cos(2\pi hu)\cos(2\pi lw)+\sin(2\pi hu)\sin(2\pi lw)\right].$$

By rearrangement and collection of terms, the Patterson function for the zero-level projection could be written as

$$P = 4/A\sum_{0}^{\infty}\sum\left\{\left[|F_{h0l}|^2+|F_{\bar{h}0l}|^2\right]\cos(2\pi hu)\cos(2\pi lw)-\left[|F_{h0l}|^2-|F_{\bar{h}0l}|^2\right]\sin(2\pi hu)\sin(2\pi lw)\right\}.$$

Thus it was possible to evaluate numerically the Patterson function at intervals of 1/60 in u and w by means of the Beevers-Lipson strips. A Patterson map was then constructed by drawing contour lines which connected points of equal "heights".

The estimation and subsequent processing of all of the spot intensities were completed at about the same time that the BXFS computer program was finished (Carpenter and Wilmot, 1962). It provides a rapid means of evaluating the crystallographic functions usually expressed in terms of the Fourier series, such as the Patterson, electron density, difference Patterson, and difference electron density functions. In the program, the Fourier synthesis is evaluated in the form

$$\sum_{h}\sum_{k}\sum_{l}G(hkl)\begin{pmatrix}\cos\\ \sin\end{pmatrix}2\pi hx\begin{pmatrix}\cos\\ \sin\end{pmatrix}2\pi ky\begin{pmatrix}\cos\\ \sin\end{pmatrix}2\pi lz,$$

where G(hkl) is a linear combination of either structure factors or differences between structure factors, or squared structure

factor magnitudes, or differences between squared structure factor magnitudes. In order to obtain the Patterson function in this form, the general form was transformed as will now be explained.

For space group $P2_1/c$, where k+l=2n (n being an integer), $F^2_{hkl} = F^2_{\bar{h}kl}$ and $F^2_{hkl} = F^2_{h\bar{k}\bar{l}}$. For the case where k+l=2n+1, again $F^2_{hkl}=F_{h\bar{k}l}$ and $F^2_{hkl} = F^2_{hk\bar{l}}$ (International Tables, 1952, p. 383). Obviously, it was sufficient to deal only with the case for which k+l=2n. In this case the summation may be split and the trigonometric identity $\cos(\alpha+\beta) = \cos\alpha\cos\beta - \sin\alpha\sin\beta$ applied to yield

$$P=1/2V\sum\sum_{-\infty}^{+\infty}\sum\Big\{F^2_{hkl}\left[\cos2\pi(hu+lw)\cos2\pi kv - \sin2\pi(hu+lw)\sin2\pi kv\right] +$$
$$F^2_{\bar{h}kl}\left[\cos2\pi(hu+lw)\cos2\pi(-kv)-\sin2\pi(hu+lw)\sin2\pi(-ky)\right]+$$
$$F^2_{h\bar{k}l}\left[\cos 2\pi(-hu+lw)\cos2\pi kv - \sin2\pi(-hu+lw)\sin2\pi kv\right] +$$
$$F^2_{h\bar{k}\bar{l}}\left[\cos2\pi(hu-lw)\cos2\pi kv - \sin2\pi(hu-lw)\sin2\pi kv\right]\Big\}.$$

After combining terms, and noting that the case k=2n+1 yields the same results, the expression for the Patterson function could be written as

$$P=4/V\sum\sum_{o}^{+\infty}\sum\Big\{F^2_{hkl}\cos2\pi(hu+lw)+F^2_{\bar{h}kl}\cos2\pi(hu-lw)\Big\}\cos2\pi kv.$$

When the trigonometric identities $\cos(\alpha+\beta) = \cos\alpha\cos\beta - \sin\alpha\sin\beta$ and $\cos(\alpha-\beta) = \cos\alpha\cos\beta + \sin\alpha\sin\beta$ were applied, and the resultingterms were combined, the Patterson function was written as

$$P=4/V\sum\sum_{o}^{\infty}\sum\Big\{\left[F^2_{hkl} + F^2_{\bar{h}kl}\right]\cos(2\pi hu)\cos(2\pi kv)\cos(2\pi lw)$$
$$-\left[F^2_{hkl}-F^2_{\bar{h}kl}\right]\sin(2\pi hu)\cos(2\pi kv)\sin(2\pi lw)\Big\}.$$

With the Patterson function in this form, it was possible to obtain a three-dimensional Patterson synthesis using

the BXFS program. Layers of the Patterson synthesis upon which important peaks were located were mapped for closer study.

3. Interpreting the Patterson Synthesis

a. The Patterson Projection, P(u,w)

The map of the zero-level Patterson projection showed only a few large, well-defined peaks, each of these peaks being of one of two different heights. It was assumed that the larger of the two kinds of peaks represented a bromine-bromine interatomic vector, and that the smaller peak represented a sodium-bromine interatomic vector. Based upon these assignments, two dimensional coordinates for the bromine and sodium atoms were found. A structure factor calculation showed the discrepancy factor, R, to be 0.387. (See section III C3 for a discussion of this type of calculation and the resulting R-value.) The construction of the zero-level Patterson projection map did serve as a rough guide in locating bromine-bromine peaks on the three-dimensional Patterson maps, but had there been computer facilities initially available for the ready evaluation of the three-dimensional synthesis, the projection would have been completely unnecessary.

b. The Three-Dimensional Patterson Synthesis

The advantage of employing a three-dimensional Patterson synthesis lies in that the resulting peaks (for a simple crystal) usually do not seriously overlap.

The three-dimensional Patterson showed three

very large peaks, in addition to the usual origin peak, which were located at u=25/60, v=14/60, w=35/60; u=0/60, v=16/60, w=30/60; and u=25/60, v=30/60, w=5/60. It was assumed that, since bromine has by far the largest atomic number of the elements present in sodium bromide dihydrate, these peaks were most probably representative of bromine-bromine interatomic vectors. Tentative coordinates for the bromine atom were obtained by the following reasoning.

The general equivalent positions of the space group $P2_1/c$ are x,y,z; $x,\frac{1}{2}-y,\frac{1}{2}+z$; $\bar{x},\frac{1}{2}+y,\frac{1}{2}-z$; and $\bar{x},\bar{y},\bar{z}$. Position x,y,z could be chosen arbitrarily as a starting point for formulating predicted interatomic vectors. The interatomic vectors $1-2x,1-2y,1-2z$; $1-2x,\frac{1}{2},\frac{1}{2}-2z$; and $0,\frac{1}{2}-2y,\frac{1}{2}$ would then be expected to appear on the Patterson sections. Now if the peak located at u=0/60, v=16/60, w=30/60 corresponds to the predicted peak at $0,\frac{1}{2}-2y,\frac{1}{2}$, then $30/60-2y=16/60$, and y=7/60. In like manner, if the peak located at u=25/60, v=30/60, w=5/60 corresponds to the predicted peak at $1-2x,\frac{1}{2},\frac{1}{2}-2z$, then x and z should be 17.5/60 and 12.5/60, respectively. Thus, with the general coordinates of the bromine atom being tentatively established as x=17.5/60, y=7/60, z=12.5/60, it was possible to predict that the third bromine-bromine vector should appear at u=25/60, v=14/60, w=35/60 (that is, at $1-2x,1-2y,1-2z$). The third of the peaks did, indeed, appear at that position. This postulated structure was tested by means of a structure factor calculation as explained in the next section.

C. Locating Atomic Positions in the Trial Structure

1. The Structure Factor

The structure factor F_{hkl}, a function of indices hkl, may be written in general as $F_{hkl} = \sum_{j=1}^{N} f_j \exp 2\pi i(hx_j+ky_j+lz_j)$. The scattering factor, f_j, for the jth atom of the N atoms present in the unit cell, is a function of the number and distribution of the electrons in the atom; it also depends upon $\sin\theta/\lambda$, where θ is the Bragg angle, and λ is the wavelength of the X-radiation employed in the diffraction experiment. The modulus of F_{hkl} is "the ratio of the amplitude of the radiation scattered in the reflection hkl by the contents of one unit cell to that scattered by a single electron under the same conditions" (Lipson and Cochran, 1953, p. 11).

2. The Temperature Factor

When discussing a crystal structure, it must be realized that the atoms involved, far from remaining stationary, undergo thermally-induced motion. This means simply that the electrons of an atom are "spread out" over a larger volume in space than they would occupy if the atom were at rest. The scattering factor curve for the atom-in-thermal-motion thus decreases more rapidly, as $\sin\theta/\lambda$ increases, than it would if the atoms were at rest. An approximate correction to be applied to the scattering factor is the Debye-Waller correction, so that $f=f_o e^{-B\sin^2\theta/\lambda^2}$ (Buerger, 1960, p. 231-232), where f is the modified scattering factor for a given atom, f_o is

the scattering factor for that stationary atom, and B is denoted as the temperature coefficient or as the isotropic temperature factor for the atom. (B is generally different for each of the different kinds of atoms in a structure.)

Thermal motion may be considered to be significantly anisotropic as well as different for each kind of atom. It is possible to convert an isotropic temperature factor into its corresponding anisotropic temperature factors by the relation

$$B(\sin^2\theta/\lambda^2) = \beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{23}kl + \beta_{31}lh$$
$$= (Ba^{*2}/4)h^2 + (Bb^{*2}/4)k^2 + (Bc^{*2}/4)l + (Ba^*b^*\cos\gamma^*/2)$$
$$+ (Bb^*c^*\cos\alpha^*/2) + (Bc^*a^*\cos\beta^*/2).$$

By equating coefficients of h^2, k^2, l^2, hk, kl, and lh, one may evaluate the β's in terms of B and the usual reciprocal cell constants. For example, $\beta_{11} = (Ba^{*2}/4)$, $\beta_{22} = (Bb^{*2}/4)$,... These relations are useful in that very often, for purposes of refinement, it is desired to allow the anisotropic factors corresponding to a known isotropic factor to vary independently, as in a least squares refinement, or in difference map refinement. The variation of these factors will depend, of course, upon the extent to which the atoms undergo anisotropic thermal motion; it will also depend upon whether or not certain undetected or uncorrected systematic errors remain in the structure factor data.

3. The Structure Factor Calculation and the R-Value

If, for a particular crystal structure, the calculated structure factor magnitudes approximately match the

observed structure factor magnitudes, it usually indicates that the correct model for that crystal structure has been proposed. Therefore, the structure factor calculation is useful as a means of testing whether or not a reasonable approximation to the crystal structure has been made.

It has been customary to regard the crystallographic discrepancy factor, R, defined as $R = \frac{\sum||F_o| - |F_c||}{\sum|F_o|}$ as an indication of the correctness of a structure. Subscripts "o" and "c" refer to observed and calculated values of $|F|$, while the summation is taken over all available reflections. It is not unusual to begin refinement of a tentative structure with an R-value of 0.40, and to work down to a highly-refined structure with an R-value in the neighborhood of 0.05-0.10. But it must be emphasized that the R-value need not necessarily be accepted at its face value. Other residuals have been suggested as measures of discrepancy, among them being Booth's residual, $R = \frac{\sum||F_o| - |F_c||^2}{\sum|F_o|^2}$, shown here as an example. For a fuller discussion of the above, see Buerger's book (1960, pp. 585-589). In this study, a weighted R-value $R_w = \sqrt{\frac{\sum||F_o| - |F_c||^2}{\sum \omega|F_o|^2}}$, is calculated in addition to the conventional R-value. The weight, w, is obtained from the equation $w = 1/\sigma^2$, where σ is the estimated standard deviation in $|F|$. Usually in judging the accuracy of a crystal structure model, it is very helpful to compare the individual calculated structure factors with their experimentally-obtained values.

For convenience in calculation, the form of F_{hkl} (given above) is usually modified by taking advantage of the space group symmetry of the crystal, as is illustrated below for $P2_1/c$. The four general equivalent positions of this space group are x,y,z; $x,\frac{1}{2}-y,\frac{1}{2}+z$; $\bar{x},\frac{1}{2}+y,\frac{1}{2}-z$; $\bar{x},\bar{y},\bar{z}$. The structure factor, F_{hkl}, may then be written as

$$F_{hkl} = \sum_{j=1}^{N/4} \sum_{\alpha=1}^{4} f_j A_{j,\alpha,hkl} \text{ , where } A_{j,\alpha,hkl} = e^{2\pi i(hx_{j,\alpha}+ky_{j,\alpha}+lz_{j,\alpha})}$$

and α refers to one of the number of atoms of kind j. The summation over α may be evaluated in the following manner:

$$\sum_{\alpha=1}^{4} A_{j,\alpha,hkl} = e^{2\pi i(hx_j+ky_j+lz_j)} + e^{-2\pi i(hx_j+ky_j+lz_j)}$$
$$+ e^{2\pi i(hx_j+k(\frac{1}{2}-y_j)+l(\frac{1}{2}+z_j))}$$
$$+ e^{-2\pi i(hx_j+k(\frac{1}{2}-y_j)+l(\frac{1}{2}+z_j))}.$$

Since the general relation, $e^{ix} = \cos(ax)+i\sin(ax)$ holds, the preceding expression may be simplified to yield

$$\sum_{\alpha=1}^{4} A_{j,\alpha,hkl} = 2\cos(2\pi[hx_j+ky_j+lz_j])$$
$$+2\cos(2\pi[hx_j-ky_j+lz_j+(k+l)/2)).$$

Application of the identity $\cos\alpha+\cos\varphi = 2\cos(\frac{1}{2}(\alpha+\varphi))\cos(\frac{1}{2}(\alpha-\varphi))$ produces $\sum_{\alpha=1}^{4} A_{j,\alpha,hkl} = 4\{\cos\frac{1}{2}(4\pi(hx_j+lz_j)+2\pi(k+l)/2)\cos\frac{1}{2}(4\pi ky_j-2\pi(k+l/2))\}$, which may be simplified to $4\cos2\pi(hx_j+lz_j+(k+l)/4)\cos2\pi(ky_j-(k+l)/4)$. Thus the structure factor is $F_{hkl} = 4\sum_{j=1}^{N/4} f_j\cos2\pi(hx_j+lz_j+(k+l)/4)\cos2\pi(ky_j-(k+l)/4)$. A further simplification may be obtained by splitting the summation into two portions, depending upon whether $(k+l)$ is even or odd, then applying simple trigonometric identities.

The results are

$$F_{hkl} = 4 \sum_{j=1}^{N_A}{}^{h+k=2n} f_j \left[\cos(2\pi hx_j)\cos(2\pi ky_j)\cos(2\pi lz_j) - \sin(2\pi hx_j)\cos(2\pi ky_j)\sin(2\pi lz_j)\right], \text{ and}$$

$$F_{hkl} = -4 \sum_{j=1}^{N_A}{}^{h+k=2n+1} f_j \left[\sin(2\pi hx_j)\sin(2\pi ky_j)\cos(2\pi lz_j) + \cos(2\pi hx_j)\sin(2\pi ky_j)\sin(2\pi lz_j)\right].$$

In these mathematical forms, the values of the structure factors may be efficiently calculated using standard tables of $\sin(2\pi hx)$ and $\cos(2\pi hx)$ (International Tables, 1959, Sec.8).

In practice, however, all structure factor calculations were performed by computer means. Two computer programs were utilized--the Pittsburgh Structure Factor Program (Shiono, 1962), a means to calculate rapidly structure factors with isotropic temperature factors only, and the BXLS Program (Carpenter, 1963), which facilitates the calculation of structure factors with anisotropic temperature parameters. The BXLS program output also provides values of (F_o-F_c) for all hkl reflections, which may then be used as Fourier coefficients for a difference Fourier synthesis if so desired. Tables of atomic scattering factors, obtained by quantum-mechanical calculations from self-consistent or variational wave functions are readily available for the sodium cation, bromine anion and oxygen atom (International Tables, 1962, pp. 202-207).

A structure factor calculation was made using only the tentative coordinates of the bromine atom; an isotropic temperature factor parameter for bromine was assumed to be 2.0Å^2. The R-value of the calculation was 0.258, indicating that a reasonable model had indeed been proposed, also that a good deal of the X-ray

scattering in the unit cell of sodium bromide dihydrate is due to the bromine ion only. From the calculation, the tentative assignment of phases (positive or negative signs in this case) to the observed structure factors could be made. Knowledge of both the magnitudes and the phases of the observed structure factors made possible the construction of a three-dimensional electron density map.

4. The Electron Density Calculation

As mentioned earlier, the general expression for the electron density evaluated at point x,y,z in the unit cell is $\rho(x,y,z) = 1/V \sum \sum_{-\infty}^{+\infty} \sum F_{hkl} e^{-2\pi i(hx+ky+lz)}$ (Lipson and Cochran, 1953, p.12), the summation being performed over indices hkl. Since the crystal under investigation is centosymmetric, the form $\rho(x,y,z) = 1/V \sum \sum_{-\infty}^{+\infty} \sum F_{hkl} \cos 2\pi(hx+ky+lz)$ is easily obtained, as in the treatment of the three-dimensional Patterson function (see III B1). The sum was split into two portions, one for the case of indices k+l = 2n, and another for the case of indices k+l = 2n+1. Use of the identities $F_{hkl} = F_{h\bar{k}l}$, $F_{\bar{h}kl} = F_{hk\bar{l}}$ for k+l = 2n, and $F_{hkl} = -F_{h\bar{k}l}$, $F_{\bar{h}kl} = -F_{hk\bar{l}}$ for k+l = 2n+1, coupled with the application of standard trigonometric identities, led to the following form of the electron density function suitable for computer calculation.

$$\rho(x,y,z) = 4/V \sum_{0}^{\infty} \sum \sum^{k+l=2n} \{[F_{hkl}+F_{\bar{h}kl}]\cos(2\pi hx)\sin(2\pi ky)\sin(2\pi lz) + [F_{\bar{h}kl}-F_{hkl}]\sin(2\pi hx)\sin(2\pi ky)\cos(2\pi lz)\}$$

$$-4/V \sum_{0}^{\infty} \sum \sum^{k+l=2n+1} \{[F_{hkl}+F_{\bar{h}kl}]\cos(2\pi hx)\sin(2\pi ky)\sin(2\pi lz) + [F_{hkl}-F_{\bar{h}kl}]\sin(2\pi hx)\sin(2\pi ky)\cos(2\pi lz)\}.$$

5. Obtaining Atomic Coordinates.

Four separate peaks appeared on the first three-dimensional electron density map. By examination of the relative peak heights, it was possible to label the peaks unambiguously as bromine, sodium and the two oxygens. It was found convenient to locate peak centers by an approximation method (Carpenter and Donahue, 1950). The coordinates of these peak centers were taken as the tentative coordinates of the four atoms. After a second structure factor calculation was made, using these coordinates together with an assumed isotropic temperature factor of 2.0$\AA^2$ for all the atoms, the R-value was a much-improved 0.127. This second calculation provided an improved set of structure factor signs for a second electron density calculation which, in turn, provided improved atomic coordinates for a third structure factor calculation. After the results of the third calculation were examined, it was apparent that there were no further changes to be made in the assignments of phases to the structure factors. (The above procedure is often referred to as the method of refinement by Fourier cycles (Buerger, 1960, pp. 590-593).) A few more factor calculations led to the adjustment of the overall isotropic temperature factor, from its initial value of 2.0$\AA^2$ to the value 2.5$\AA^2$. As indicated by the R-value of 0.103, there was, at this point, fair agreement between calculated and observed structure factors. In order to refine the structure further, it was decided to employ the

three-dimensional difference synthesis.

D. Refining the Trial Structure

1. The Difference Electron Density Calculation

The general expression for the electron density using the experimentally-derived structure factor values as Fourier coefficients may be written as $\rho_o = 1/V\sum\sum_{-\infty}^{+\infty}\sum F_o e^{-2\pi i(hx+ky+lz)}$, where subscript "o" indicated "observed". If structure factors based upon a proposed model of the crystal structure are used as Fourier coefficients, the electron density may also be expressed as $\rho_c = 1/V\sum\sum_{-\infty}^{+\infty}\sum F_c e^{-2\pi i(hx+ky+lz)}$, where subscript "c" indicates "calculated". If ρ_c is subtracted from ρ_o, the expression $(\rho_o - \rho_c) = 1/V\sum\sum_{-\infty}^{+\infty}\sum (F_o-F_c)e^{-2\pi i(hx+ky+lz)}$ results; it is a general expression of the difference electron density function, utilizing (F_o-F_c)'s as Fourier coefficients. The form of $(\rho_o - \rho_c)$ suitable for computer calculation may be obtained by employing exactly the same procedure as was used in dealing with the electron density function.

If the trial structure exactly matches the real structure, the difference map should be absolutely featureless, but, in reality, random fluctuations will appear owing to observational errors. If, however, the trial structure differs in some systematic way from the real structure, the difference map will often exhibit that difference, and, in so doing, will indicate the direction in which improvements of atomic parameters should be carried out in order to produce a more nearly

featureless map.

2. Correction of Coordinate Errors by Difference Maps

If a postulated atomic location is only moderately in error, the difference map will reveal it to be situated upon a steep gradient. There is a convenient semi-empirical formula used to evaluate the magnitude of the correction. It is the relation $\epsilon = \frac{d(\rho_o - \rho_c)}{dr} \Big/ 2\,\rho_o(0)p$ (Buerger, 1960, pp. 604-606), where ϵ is the coordinate correction, r is the distance from the atomic center, $\frac{d(\rho_o - \rho_c)}{dr}$ is the slope of $(\rho_o - \rho_c)$ in the immediate neighborhood of the center, and $\rho_o(0)$ is the maximum electron density given approximately by $\rho_o(0) = Z(p/\pi)^{3/2}$, Z denoting the atomic number and p being about 5.0. The fractional coordinate corrections carried out for the bromine, sodium and two oxygen atoms were all quite small, none exceeding 0.002.

3. Adjustment of Anisotropic Temperature Factors by Difference Maps

On the difference map, anisotropy in the thermal motion of an atom will generally be evidenced by the appearance of a saddle-shaped region about the atomic center. (As previously mentioned, this appearance might also be traced to the presence of systematic errors in the structure factor data.) Some relatively large adjustments had to be made in the temperature parameters of bromine, sodium and the two oxygens. After adjustments based upon four difference maps had been carried out, it

was judged that the expense of computer operation and the time involved in the determination of smaller and smaller parameter adjustments seemed not to warrant further refinement by this method. A good general discussion of the difference synthesis is given by Buerger (1960, pp. 603-609) and Lipson and Cochran (1953, pp. 208-306).

For the final refinement of the crystal structure, a least squares method seemed most suitable.

4. Least Squares Refinement

The BXLS computer program, which carries out refinement by least squares, minimizes essentially the function $R_w = \frac{\sum w | K|Fo| - |Fc||^2}{\sum w |K|Fo||^2}$ (Carpenter, 1963). The minimization of R_w led to changes in all of the atomic parameters. After two cycles of least squares were completed, a difference map was constructed. The map showed marked improvement in that it was much more nearly featureless than previous ones. After the third cycle of least squares, however, it was evident that the parameter values had converged, that is, the changes in the parameters were insignificantly small. At that point it was judged that the refinement was completed.

A total of 506 reflections were employed throughout the course of refinements; no "unobserved" reflections were utilized. (an unobserved reflection is one which has a corresponding intensity value less than a certain observable minimum.) The comparisons between the observed and calculated structure factors, for all

the available hkl reflections, are listed in the Appendix of this thesis.

The effects of the difference map and least-squares refinements upon the atomic parameters and other structural quantities which resulted from Fourier refinement, are shown in Table II. It should be remembered that the difference map refinement was not carried as far as it should have been.

TABLE II

Effects of Difference Map and Least-Squares Refinement upon Atomic Parameters and Other Structural Quantities

Parameter	Fourier Refinement	Diff. Map Refinement	Least Sq. Refinement
		Bromine	
x	0.2962	0.2969	0.2964
y	0.1194	0.1195	0.1191
z	0.2117	0.2123	0.2119
β_{11}	0.01718	0.02406	0.02404
β_{22}	0.00572	0.00800	0.00841
β_{33}	0.01615	0.01939	0.01861
β_{12}	0.0	0.0	0.0
β_{23}	0.0	0.0	0.0
β_{31}	0.01322	0.01851	0.01875
		Sodium	
x	0.0150	0.0146	0.0146
y	0.1680	0.1684	0.1693
z	0.4567	0.4568	0.4567
β_{11}	0.01718	0.02406	0.02525
β_{22}	0.00572	0.00800	0.00772
β_{33}	0.01615	0.01939	0.01798
β_{12}	0.0	0.0	0.0
β_{23}	0.0	0.0	0.0
β_{31}	0.01322	0.01851	0.01263

TABLE II (continued)

Parameter	Fourier Refinement	Diff. Map Refinement	Least Sq. Refinement
	Oxygen (I)		
x	0.7940	0.7940	0.7882
y	0.3110	0.3118	0.3132
z	0.1780	0.1774	0.1762
β_{11}	0.01718	0.02268	0.02052
β_{22}	0.00572	0.00755	0.00831
β_{33}	0.01615	0.02132	0.02213
β_{12}	0.0	0.0	0.0
β_{23}	0.0	0.0	0.0
β_{31}	0.01322	0.01746	0.00911
	Oxygen (II)		
x	0.2129	0.2139	0.2130
y	0.4929	0.4914	0.4900
z	0.2218	0.2203	0.2199
β_{11}	0.01718	0.02268	0.02063
β_{22}	0.00572	0.00755	0.00833
β_{33}	0.01615	0.02132	0.02292
β_{12}	0.0	0.0	0.0
β_{23}	0.0	0.0	0.0
β_{31}	0.01322	0.01746	0.01608

TABLE II (continued)

Other Quantities

Quantity	Fourier Refinement	Diff. Map Refinement	Least Sq. Refinement
K(scale factor)	4.40469	3.91000	3.89510
R-value	0.103	0.065	0.0615
R_w-value	0.133	0.077	0.0707

Note: The anisotropic parameters β_{12} and β_{23} are required to be equal to zero since, for the monoclinic crystal, $\cos\alpha^* = \cos\gamma^* = 0$ (see III C 2). Therefore, these parameters were held invariant throughout the structure refinement.

IV. Description and Discussion of the Structure

A. General Structural Features

Figure 1* is a projection, on the a-c plane, of the crystal structure of sodium bromide dihydrate. The numbers in parentheses are fractional coordinates which indicate distances along the b axis. The structure may be described as composed of separate layers parallel to the b-c plane. Each of these layers may be subdivided into three sheets of atoms containing, respectively, bromine and oxygen, sodium, and bromine and oxygen. As will be more fully discussed later, the separate layers appear to be held together largely by hydrogen bonds, thus accounting for the ready cleavage of this hydrate in the b-c plane (Van Meersche et al, 1962).

Alternately, one may regard the layers as being constructed from a series of octahedra, with the sodium cation at the center of each octahedron. The sodium cation is coordinated to four oxygen atoms and to two bromine anions, but each bromine anion and each oxygen atom is also coordinated to an adjoining sodium cation. Thus, since each electronegative atom is shared between two adjoining octahedra, the cohesion within the layers parallel to the b-c plane is explained (see Figure 2A).

* The figures are on pages 54 and 56.

B. Discussion of Interatomic Distances

Based upon the coordinates of the sodium, bromine and two oxygen atoms which resulted from least-squares refinement, and the unit cell dimensions, it was possible, with the aid of an "Interatomic Distances" computer program (Carpenter and Hall, 1962) to obtain all the relevant interatomic distances in the sodium bromide dihydrate crystal. These distances are listed below with their standard deviations in parentheses. The standard deviations were calculated from the equation for variance, $\sigma^2_{D_{12}} = \sum_i \left(\frac{\partial D_{12}}{\partial x_i}\right)^2 \sigma^2_{x_i}$ where D_{12} refers to the distance between atom 1 and atom 2, $\left(\frac{\partial D_{12}}{\partial x_i}\right)$ is the partial derivative with respect to the ith coordinate. (The variance, $\sigma^2_{x_i}$ is the square of the standard deviation obtained from BXLS output; it is an estimate of internal data consistency only.)

The distances of 2.963Å (0.005Å) and 2.983Å(0.006Å) between the sodium and bromine ions are consistent with the sum of their crystal radii, 2.90Å (Pauling, 1960, p. 514). The two distances are almost identical with that observed in the sodium bromide crystal, 2.98Å. The sodium ion-oxygen atom distances of 2.401Å(0.009Å), 2.410Å(0.009Å), 2.418Å(0.009Å), and 2.495Å(0.11Å) are also in good accord with the predicted value of 2.35Å based upon Pauling's crystal radii (see Figure 2A).

The shortest oxygen-bromine ion distances are 3.355Å(0.008Å), 3.356Å(0.009Å), and 3.383Å(0.010Å). The sum of the van der Waals radii of these atoms is 3.35Å (Pauling, 1960, p. 260). The next shortest bromine-oxygen

interatomic distance is 3.575Å(0.007Å). An important oxygen-bromine-oxygen angle is 103.33°(0.27°) (see Figure 1).

The following interatomic distances and angles refer only to atoms which belong to one octahedron. Bromine-oxygen distances vary from 3.806Å(0.009Å) to 3.920Å(0.009Å), oxygen-oxygen lengths range from 3.185Å (0.009Å) to 3.637Å(0.013Å), and the two bromine ions are 4.356Å(0.002Å) apart. The angle formed by the sodium cation and the two bromine anions is 94.22°(0.17°), while the oxygen-sodium-oxygen and oxygen-sodium-bromine angles vary from 82.92°(0.42°) to 95.50°(0.57°) (see Figure 2B).

C. Comparison Between This Structure Determination and Van Meerssche's

The structure of sodium bromide dihydrate just described is almost exactly that worked out by Van Meerssche and co-workers (1962). This development presented a rare opportunity for a comparison of two completely independent, yet contemporary, structure determinations of the same substance. There is, in general, good agreement between the atomic coordinates determined here and those reported by Van Meerssche and co-workers at the Université de Louvain in Belgium. But in order to arrive at a more detailed comparison of the two structure determinations, it was decided to subject Van Meerssche's data to the BXLS least-squares program previously mentioned. In this treatment, the weights assigned to Van Meerssche's structure factor data were based upon those employed in this study. In addition, his isotropic temperature factors

were converted to anisotropic temperature factors, which were then allowed to vary independently along with the coordinates and scale factor. In essence, the final refinements of the two sets of data resulting from the two separate studies were identical. Table III is presented for purposes of comparison.

It may be readily seen that by allowing each of the anisotropic temperature factors to vary, slight changes appear in the coordinates originally reported by Van Meerssche. Indeed, these changes, on the whole, lead to less agreement between the two sets of coordinates. In most cases, however, the altered coordinates do not differ from those obtained in this study by more than 2σ, where σ is an estimated standard deviation obtained from the BXLS program output. To be more specific: Of the twelve coordinates, six agree within the range of $0 - \sigma$, four within $\sigma - 2\sigma$, and two within $2\sigma - 3\sigma$.

No useful comparison, however, can be made between the two sets of anisotropic temperature factors, owing to the different absorption errors in both sets of structure factor data. This point is more fully discussed in the following paragraphs.

TABLE III

Structural Parameters from Brown University and from the Universite de Louvain, after BXLS Refinement

Bromine

Note: The figures in parentheses are standard deviations obtained from BXLS output.

Parameter	Brown University	Université de Louvain reported	Université de Louvain after BXLS
x	0.2964 (0.00017)	0.2965	0.2965 (0.00020)
y	0.1191 (0.00013)	0.1191	0.1192 (0.00014)
z	0.2119 (0.00018)	0.2120	0.2120 (0.00021)
β_{11}	0.02404(0.00024)	0.02197 (B=3.19)	0.01995(0.00032)
β_{22}	0.00841(0.00012)	0.00740	0.00704(0.00015)
β_{33}	0.01861(0.00022)	0.02063	0.02020(0.00033)
β_{12}	0.00000(0.00000)	0.00000	0.00000(0.00000)
β_{23}	0.00000(0.00000)	0.00000	0.00000(0.00000)
β_{31}	0.01875(0.00034)	0.01698	0.01539(0.00049)
	Sodium		
x	0.0146 (0.00067)	0.0155	0.0159 (0.00075)
y	0.1693 (0.00049)	0.1679	0.1683 (0.00050)
z	0.4566(0.00069)	0.4576	0.4579 (0.00075)
β_{11}	0.02525(0.00117)	0.02169 (B=3.15)	0.02198(0.00116)
β_{22}	0.00772(0.00050)	0.00731	0.00465(0.00045)
β_{33}	0.01798(0.00108)	0.02037	0.01748(0.00113)
β_{12}	0.00000(0.00000)	0.00000	0.00000(0.00000)
β_{23}	0.00000(0.00000)	0.00000	0.00000(0.00000)
β_{31}	0.01263(0.00180)	0.01676	0.01610(0.00173)

TABLE III (continued)

Parameter	Brown University	Université de Louvain reported	Université de Louvain after BXLS
Oxygen (I)			
x	0.7882 (0.00122)	0.7907	0.7915 (0.00131)
y	0.3132 (0.00091)	0.3132	0.3138 (0.00102)
z	0.1762 (0.00129)	0.1761	0.1770 (0.00149)
β_{11}	0.02052(0.00184)	0.02472 (B=3.59)	0.01924(0.00209)
β_{22}	0.00831(0.00095)	0.00833	0.00580(0.00091)
β_{33}	0.02213(0.00211)	0.02321	0.02367(0.00233)
β_{12}	0.00000(0.00000)	0.00000	0.00000(0.00000)
β_{23}	0.00000(0.00000)	0.00000	0.00000(0.00000)
β_{31}	0.00911(0.00302)	0.01911	0.01497(0.00328)
Oxygen (II)			
x	0.2130 (0.00112)	0.2162	0.2154 (0.00132)
y	0.4900 (0.00084)	0.4922	0.4919 (0.00096)
z	0.2199 (0.00130)	0.2195	0.2189 (0.00143)
β_{11}	0.02063(0.00175)	0.02370 (B=3.47)	0.02100(0.00210)
β_{22}	0.00833(0.00099)	0.00805	0.00651(0.00094)
β_{33}	0.02292(0.00198)	0.02244	0.01974(0.00208)
β_{12}	0.00000(0.00000)	0.00000	0.00000(0.00000)
β_{23}	0.00000(0.00000)	0.00000	0.00000(0.00000)
β_{31}	0.01608(0.00284)	0.01847	0.01662(0.00320)

TABLE III (continued)

Quantity	Brown University	Université de Louvain reported	Université de Louvain after BXLS
R(scale factor)	3.89510	0.80	0.88290
R(obs.only)	0.0615		0.0999
R_w(obs.only)	0.0707		0.1188
R(all refl.)		0.1236 (0.114)	0.1095
R_w(all refl.)		0.1486	0.1239
Shortest O-Br Distances	3.355Å	3.32Å	3.325Å
	3.356Å	3.37Å	3.372Å
	3.383Å	3.36Å	3.362Å

Notes: β_{12} and β_{23} must be zero. (see Note at end of Table II.

The "reported" R-values of the Université de Louvain are those which resulted from a structure factor calculation using the "reported" coordinates and B-values, together with the BXLS program. The R-value in parentheses is taken directly from Van Meerssche's paper (1962).

When the two sets of coordinates were used to calculate structure factors, a comparison between the observed and calculated structure factors brought forth two interesting observations. Firstly, Van Meerssche's group has taken pains in obtaining intensity data for very weak reflections; secondly, in spite of these apparently painstaking intensity measurements, with an integrating Weissenberg goniometer, the agreement between observed and calculated structure factors was not quite as good (for the same reflections) as it was in this study (Van Meersche et al, 1962; also see Appendix).

A possible clue to the explanation of the latter observation may be found in the fact that no absorption corrections were applied either in this work or in that performed by Van Meerssche's group. The absorption correction would be more important for data obtained from the rectangular crystal and CuKα radiation employed by Van Meerssche than for the cylindrical crystal and MoKα radiation used in this thesis work. This absorption effect is noticeable in that Van Meersche's temperature factors tend to be lower than those obtained here. It appears that the higher precision in intensity measurements gained by Van Meerssche and co-workers by employing an integrating Weissenberg camera was offset by their omitting the absorption correction.

The structure of sodium bromide dihydrate proves to be isomorphous also with that of the dihydrate of sodium cyanide (Le Bihan, 1958).

D. Hydrogen Bonding in Sodium Bromide Dihydrate

Only three oxygen-bromine interatomic distances, 3.355Å, 3.356Å and 3.383Å, are short enough to be reasonably indicative of hydrogen bonds. Apparently, only three of the four hydrogen atoms present in the unit of sodium bromide dihydrate are involved in hydrogen bonding. This finding is supported by Hornig's infrared investigations (see Chap. I) and by Van Meerssche's nuclear magnetic resonance experiments. The latter indicate that nearly-rectilinear hydrogen bonds exist between those oxygen and bromine atoms separated by distances of 3.32Å, 3.37Å and 3.36Å (Van Meerssche, 1962). The six $O\text{-}Br^-$ distances just mentioned are very similar to the hydrogen bonded $O\text{-}Br^-$ distances of 3.30Å and 3.35Å in D(-) isoleucine $HBr \cdot H_2O$, and to the distance of 3.38A in 11-amino-undecanoic acid $HBr \cdot \frac{1}{2}H_2O$ (quoted by Pimental and McClellan, 1960, p. 290).

In this study, it was determined to investigate the possibility of locating the hydrogen atoms directly by examination of difference maps. It was possible to detect three peaks on the difference map which are located at about the positions where one would expect to find the hydrogen atoms involved in hydrogen bonding. The proposed locations for the three hydrogen atoms are $x = 0.317$, $y = 0.567$, $z = 0.250$; $x = 0.283$, $y = 0.422$, $z = 0.317$; and $x = 0.733$, $y = 0.395$, $z = 0.200$. The oxygen-to-peak distances were calculated to be 0.96Å, 1.02Å, and 0.97Å.. The H-O-H angle was then calculated to be 110.3° (see Figure 1).

These numbers are in fair agreement with the known parameters of the deuterium oxide molecule. From neutron diffraction work, the O-D distance is listed as 1.01Å, and the D-O-D angle is given as 109.5° (Pauling, 1960, p.468).

Unfortunately, there are many peaks appearing on the difference map which are as large as, or slightly larger than, the three peaks just mentioned. Therefore, although the three peaks in all probability indicate hydrogen atom positions, the peaks cannot be unambiguously idenfied as such.

There was no peak discernible on the difference map which could be designated as the position of the fourth hydrogen atom. Its location may even be a disordered one: even though the H-O-H angle must be maintained, there are many possible locations for the fourth, non-hydrogen-bonded hydrogen atom.

The extent of hydrogen bonding in sodium bromide dihydrate is, oddly enough, much greater than that reported to exist in the dihydrate of sodium cyanide (Le Bihan, 1958). The nitrogen atom typically shows a markedly greater tendency towards hydrogen bond formation than does the bromine atom. Hence, one would expect that at least three of the four hydrogen atoms in the cyanide (structurally isomorphous with the bromide) would be involved in hydrogen bonds. But Le Bihan found only one nitrogen-oxygen interatomic distance (2.81Å) short enough to be considered for hydrogen bonding. It should be noted, however, that the R-value for the cyanide structure is 0.19. It is

therefore difficult to assess the reliability of Le Bihan's reported interatomic distances for the only partially-refined structure. For example, there is a nitrogen-oxygen distance of 3.18Å in the structure which, after further structure refinement, might possibly be modified to a value indicative of at least a weak hydrogen bond.

In summary, this thesis work has shown that a well-refined crystal structure, even one composed of both light and heavy atoms, can provide interesting information regarding the distribution of hydrogen bonds in the structure, and the probable locations of the hydrogen atoms. It was gratifying to note the agreement between this crystal structure analysis, the infrared work done by Hornig (1961), and the structure determination carried out by Van Meerssche and co-workers (1962).

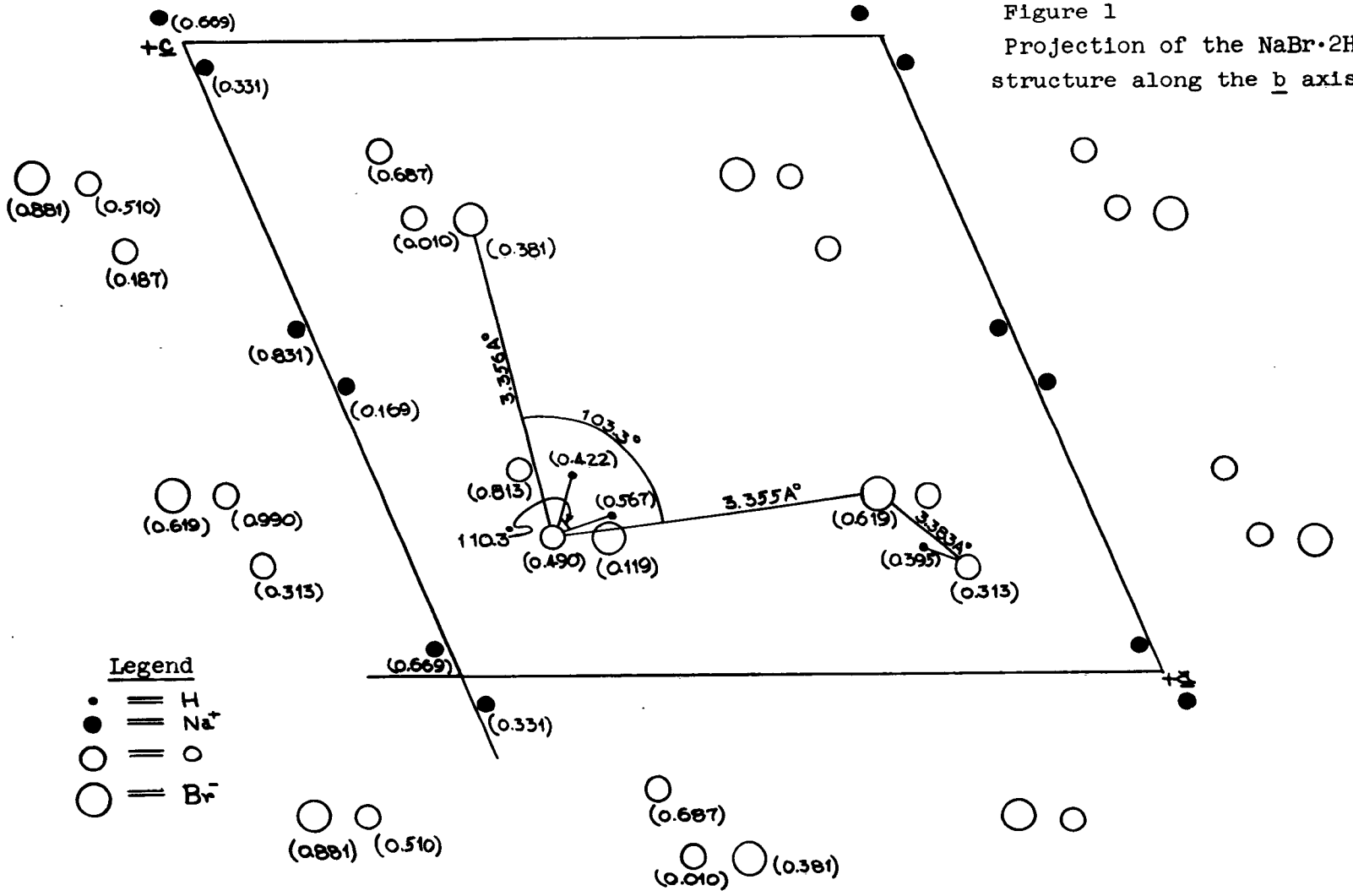


Figure 1
Projection of the $NaBr \cdot 2H_2O$ structure along the b axis

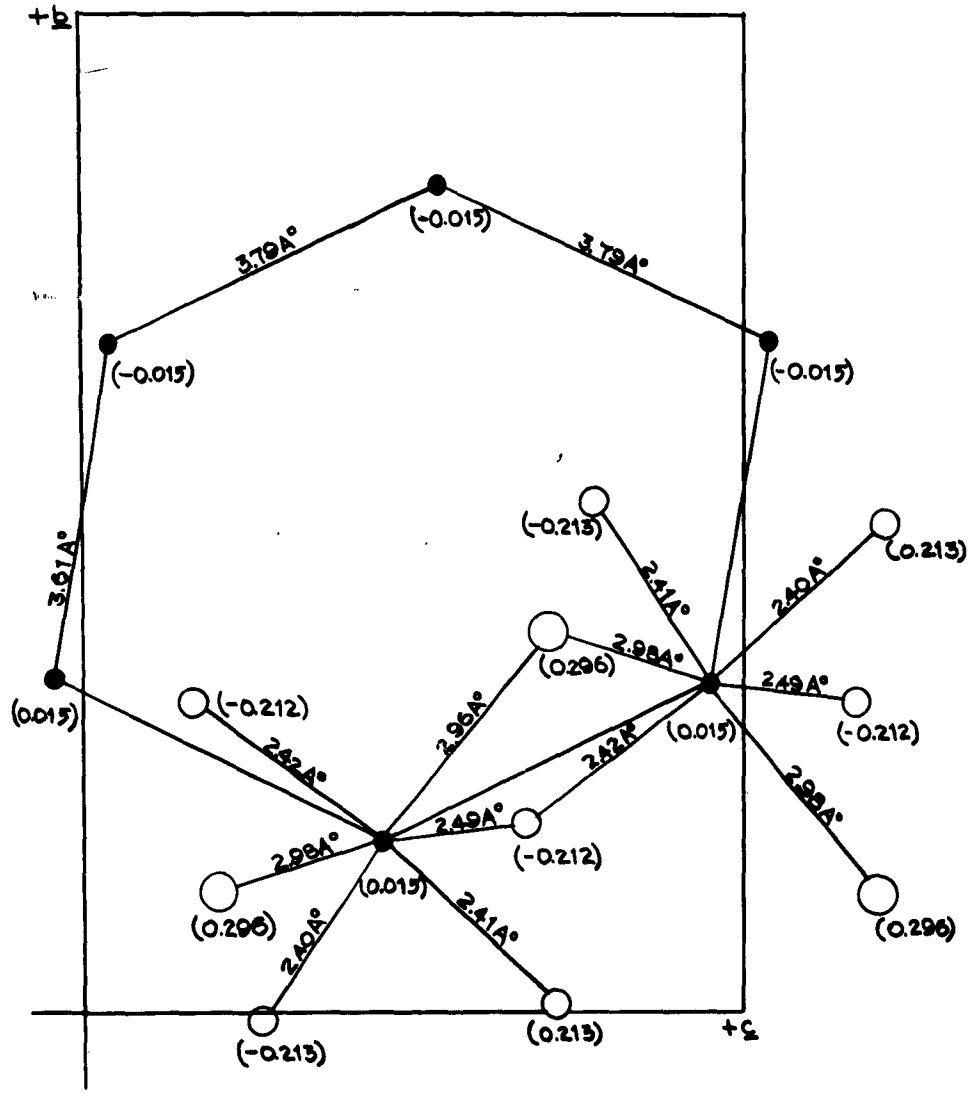
Legend

● = Na^+

○ = O

◯ = Br^-

Figure 2A
Projection of the $NaBr \cdot 2H_2O$ structure along the a axis
(only 2 octahedra shown)



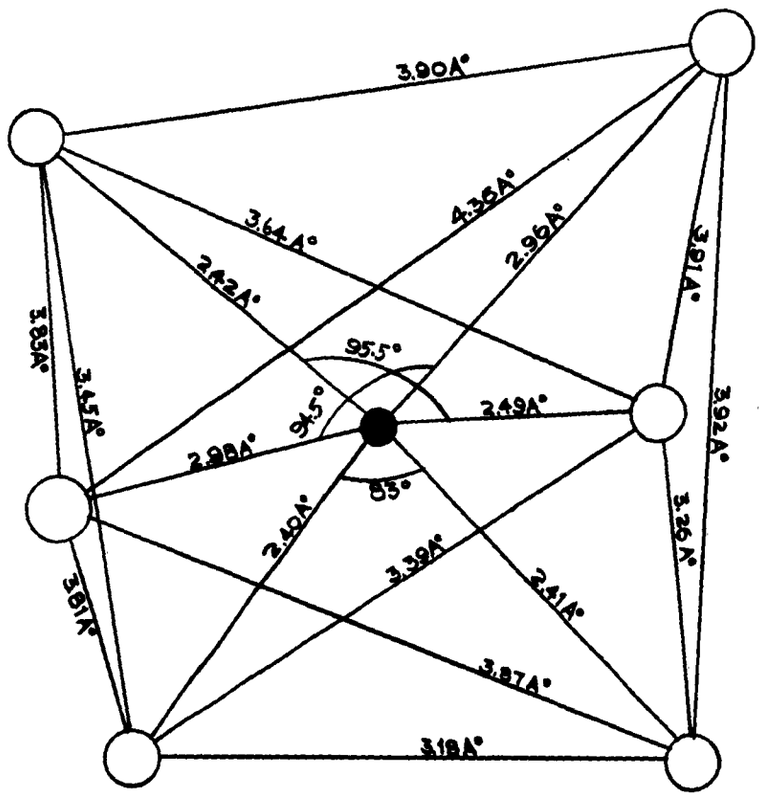
Legend

○ = Na^+

◯ = O

◯ = Br^-

Figure 2B
Dimensions of a single octahedron
(Projection along a axis)



Appendix

Notes: All F_o's prefixed by a minus sign are "unobserved". All structure factors are multiplied by 10 for convenience.

hkl	Structure Factors Obtained in This Thesis Work (after BXLS refinement) F_o	F_c	Structure Factors Given by Van Meerssche and Co-workers (1962) (after BXLS refinement) F_o	F_c
100	184	135	159	135
200	1057	- 982	865	- 991
300	666	659	653	687
400	528	529	600	548
500	213	- 216	274	- 256
600	104	101	124	118
700	150	154	194	197
002	1048	-1043	945	-1036
$10\bar{2}$	104	99	115	96
$\bar{1}02$	767	879	962	881
$20\bar{2}$	1202	1212	1210	1234
$\bar{2}02$	958	981	848	985
$30\bar{2}$	- 89	0	- 18	- 4
$\bar{3}02$	434	- 468	397	- 472
$40\bar{2}$	303	- 311	362	- 336
$\bar{4}02$	104	100	88	115
$50\bar{2}$	242	275	344	311
$\bar{5}02$	425	436	477	477
$60\bar{2}$	92	128	141	141
$\bar{6}02$	206	- 200	247	- 225
$70\bar{2}$	- 142	- 69		
$\bar{7}02$	100	- 80	106	- 104
$\bar{8}02$	185	185		
004	550	532	486	536
$10\bar{4}$	432	437	406	445
$\bar{1}04$	604	- 584	433	- 559
$20\bar{4}$	394	- 396	406	- 404
$\bar{2}04$	- 32	4	- 35	10
$30\bar{4}$	- 107	34	- 26	31
$\bar{3}04$	673	660	556	655
$40\bar{4}$	300	318	327	346
$\bar{4}04$	287	- 288	265	- 284
$50\bar{4}$			62	- 51
$\bar{5}04$	292	- 288	300	- 302
$60\bar{4}$	335	333	353	346
$\bar{8}04$	189	- 192		
006	- 76	- 34	- 44	- 31
106	288	- 300	300	- 289

hkl	F_o	F_c	F_o	F_c
$\bar{1}06$	452	443	353	424
206	137	147	177	156
$\bar{2}06$	228	- 234	230	- 213
306	131	104	106	114
$\bar{3}06$	416	- 406	424	- 392
$\bar{4}06$	293	309	230	277
$\bar{5}06$	- 81	76		
$\bar{6}06$	316	- 304		
008	61	- 98		
108	95	147		
$\bar{1}08$	201	- 236		
$\bar{2}08$	145	156		
$\bar{3}08$	- 80	83		
$\bar{4}08$	263	- 260		
$\bar{5}08$	- 78	- 4		
$\bar{6}08$	118	114		
$\bar{7}08$	88	- 126		
110	635	- 626	521	- 631
210	448	429	433	442
310	201	195	185	206
410	537	- 510	583	- 551
510	- 115	- 56	62	- 71
610	213	210	265	239
710			106	- 96
011	70	- 53	79	- 59
111	879	- 863	803	- 870
$\bar{1}11$	431	438	388	433
211	169	202	168	199
$\bar{2}11$	695	- 716	653	- 713
311	282	286	274	296
$\bar{3}11$	264	- 262	274	- 266
411	430	- 441	441	- 466
$\bar{4}11$	451	446	450	458
511	127	- 144	150	153
$\bar{5}11$	139	- 136	141	- 154
611	180	183	238	212
$\bar{6}11$	316	- 287	327	- 318
711			- 44	- 47
$\bar{7}11$			150	133
012	376	- 360	380	- 358
112	619	611	547	607
$\bar{1}12$	276	- 302	309	- 297
212	- 80	80	71	62
$\bar{2}12$	853	966	768	976
312	242	- 243	284	- 269
$\bar{3}12$	275	305	283	322
412	201	204	256	224
$\bar{4}12$	425	- 429	433	- 438

hkl	F_o	F_c	F_o	F_c
$\bar{5}12$	- 115	80	79	95
$5\bar{1}2$	156	180	221	194
$6\bar{1}2$	151	- 144	185	- 176
$\bar{6}12$	319	294	344	327
$\bar{7}12$			71	- 80
013	386	- 358	309	- 350
$1\bar{1}3$	345	349	318	346
$\bar{1}13$	270	- 273	283	- 268
$2\bar{1}3$	115	- 121	115	- 124
$\bar{2}13$	425	485	380	459
$3\bar{1}3$	399	- 394	424	- 412
$\bar{3}13$	212	- 225	203	- 238
$4\bar{1}3$	153	124	141	133
$\bar{4}13$	486	- 498	477	- 499
$5\bar{1}3$			150	133
$\bar{5}13$	276	283	291	299
$6\bar{1}3$			106	- 153
$\bar{6}13$	192	199	230	209
$\bar{7}13$	232	- 214	221	- 243
014	603	625	539	611
$1\bar{1}4$	198	- 196	185	- 195
$\bar{1}14$	417	387	397	385
$2\bar{1}4$	- 93	- 94	97	- 94
$\bar{2}14$	421	- 406	441	- 383
$3\bar{1}4$	258	280	300	288
$\bar{3}14$	199	193	177	196
$4\bar{1}4$			- 35	17
$\bar{4}14$	493	492	450	501
$5\bar{1}4$			71	- 80
$\bar{5}14$	117	- 93	62	- 72
$\bar{6}14$	- 107	- 32	- 35	- 17
$\bar{7}14$	214	194	247	218
015	292	265	212	242
$1\bar{1}5$	185	- 181	168	- 183
$\bar{1}15$	- 89	- 56	44	- 62
$2\bar{1}5$	108	- 104	106	- 105
$\bar{2}15$	388	- 378	397	- 349
$3\bar{1}5$	171	166	185	174
$\bar{3}15$	285	303	238	298
$4\bar{1}5$			- 35	- 41
$\bar{4}15$	261	272	238	258
$\bar{5}15$	317	- 332	309	- 332
$\bar{6}15$	- 104	- 61	71	- 58
$\bar{7}15$	230	219		
016	211	- 190	168	- 175
$1\bar{1}6$	168	183	194	178
$\bar{1}16$	86	90	79	91
$2\bar{1}6$	171	199	212	195

hkl	F_o	F_c	F_o	F_c
$\bar{2}16$	423	364	309	351
$\bar{3}16$			88	- 79
$\bar{3}16$	- 96	- 79	71	- 50
$\bar{4}16$	- 65	- 54	- 44	- 28
$\bar{5}16$	266	266	256	265
$\bar{6}16$	- 99	6		
$\bar{7}16$	74	- 113		
017	148	- 159		
$\bar{1}17$	106	127		
$\bar{2}17$	215	188		
$\bar{3}17$	222	- 222		
$\bar{4}17$	- 100	- 46		
$\bar{5}17$	271	258		
$\bar{6}17$	- 100	- 25		
$\bar{7}17$	155	- 120		
018	120	135		
$\bar{1}18$	- 95	- 43		
$\bar{2}18$	- 100	- 52		
$\bar{3}18$	173	176		
$\bar{3}19$	164	144		
020			- 35	- 16
120	191	- 194	212	- 200
220	316	- 270	300	- 277
320	106	- 98	97	- 88
420			- 35	- 37
520			79	- 76
620			71	- 39
720			- 35	- 10
021	1071	-1039	936	-1045
$\bar{1}21$	- 57	- 19	- 53	- 11
$\bar{1}21$	654	606	680	610
221	676	658	636	686
$\bar{2}21$	419	466	415	474
321	453	- 437	433	- 457
$\bar{3}21$	971	- 962	892	- 999
421	238	- 238	247	- 259
$\bar{4}21$	163	- 173	185	- 195
521	409	387	486	439
$\bar{5}21$	462	461	556	495
621			- 62	21
$\bar{6}21$	174	- 174	212	- 199
721			168	- 198
$\bar{7}21$	211	- 222	274	- 263
022	356	- 309	388	- 311
122	335	- 318	327	- 315
$\bar{1}22$	104	89	124	95

hkl	F_o	F_c	F_o	F_c
$\bar{2}22$			35	- 50
$\bar{2}22$	110	92	124	97
$\bar{3}22$			- 18	- 13
$\bar{3}22$	187	- 200	203	- 214
$\bar{4}22$			79	- 60
$\bar{4}22$	197	- 169	212	- 186
$\bar{5}22$			71	- 48
$\bar{5}22$			- 26	- 7
$\bar{6}22$			- 35	- 40
$\bar{6}22$			- 44	22
$\bar{7}22$			- 26	- 1
023	443	430	441	427
$\bar{1}23$	255	245	238	246
123	1110	-1019	1121	-1014
$\bar{2}23$	620	- 616	600	- 628
223	437	- 413	433	- 427
$\bar{3}23$	- 102	- 7	- 35	6
323	675	673	583	659
$\bar{4}23$	229	232	274	264
423	300	- 288	274	- 299
$\bar{5}23$	197	- 167	221	- 192
523	556	- 530	539	- 562
$\bar{6}23$	230	195	212	197
$\bar{7}23$	- 125	- 59	35	55
$\bar{8}23$	233	- 181		
024			62	70
$\bar{1}24$			106	104
124	213	- 210	256	- 219
$\bar{2}24$			79	- 84
224	220	- 188	230	- 198
$\bar{3}24$			141	- 109
324	- 73	70	88	73
$\bar{4}24$			- 26	- 24
424	112	98	106	110
$\bar{5}24$			35	5
524			- 35	- 4
$\bar{6}24$			- 35	- 45
025	340	- 317	300	- 314
$\bar{1}25$	453	- 447	441	- 441
125	486	446	415	416
$\bar{2}25$	211	212	221	216
225	197	- 203	238	- 202
$\bar{3}25$	- 117	53	62	55
325	635	- 593	592	- 583
$\bar{4}25$	197	- 201	194	- 217
425	210	223	203	189
$\bar{5}25$	119	110	97	86
$\bar{6}25$	377	- 351	370	- 367
$\bar{7}25$	- 119	- 2		

hkl	F_o	F_c	F_o	F_c
$\bar{8}25$	219	132		
026	- 79	- 45	- 44	- 46
126			71	- 73
$\bar{1}26$	90	79	79	81
226			- 26	16
$\bar{2}26$			79	74
326			26	35
$\bar{3}26$			- 44	- 19
426			- 44	- 28
$\bar{5}26$			- 26	10
027	- 123	- 56		
127	188	165		
$\bar{1}27$	314	- 314		
$\bar{2}27$	103	138		
$\bar{3}27$	- 121	116		
$\bar{4}27$	364	- 329		
$\bar{5}27$	- 122	- 15		
$\bar{6}27$	237	203		
$\bar{7}27$	86	- 121		
$\bar{8}27$	166	- 98		
$\bar{2}29$	143	- 153		
$\bar{3}29$	- 125	- 18		
$\bar{4}29$	143	158		
130	999	- 915	927	- 918
230	342	345	336	356
330	457	421	441	431
430	347	- 354	406	- 387
530	- 119	- 46	79	- 46
630	198	193	265	230
730			62	- 82
031	259	205	283	212
131	1350	1253	1244	1282
$\bar{1}31$	719	- 644	733	- 649
$\bar{2}31$	130	168	159	175
231	506	488	539	505
$\bar{3}31$	290	- 303	300	- 318
331	554	572	539	593
$\bar{4}31$	293	268	291	295
431	62	- 83	97	- 95
$\bar{5}31$	164	202	194	219
531	125	85	141	100
631			- 62	- 55
$\bar{6}31$	159	148	185	180
$\bar{7}31$			62	59
731			124	- 87
032	302	- 300	371	- 297

hkl	F_o	F_c	F_o	F_c
$\bar{1}32$	697	695	662	703
$\bar{1}\bar{3}2$	619	- 606	680	- 597
$\bar{2}32$	- 83	- 61	35	- 64
$2\bar{3}2$	514	535	645	542
$\bar{3}32$	419	- 425	450	- 446
$3\bar{3}2$	143	141	168	139
$\bar{4}32$	175	184	212	205
$4\bar{3}2$	406	- 442	450	- 463
$\bar{5}32$	140	136	185	152
$5\bar{3}2$	112	131	124	146
$\bar{6}32$	129	- 128	150	- 157
$6\bar{3}2$	206	188	256	215
$\bar{7}32$	175	- 158	177	- 185
033	421	419	468	432
$\bar{1}33$	369	- 350	353	- 354
$1\bar{3}3$	585	540	592	553
$\bar{2}33$	102	74	106	73
$2\bar{3}3$	237	- 248	265	- 239
$\bar{3}33$	409	424	459	451
$3\bar{3}3$			71	49
$\bar{4}33$			- 26	10
$4\bar{3}3$	298	320	327	339
$\bar{5}33$			88	- 88
$5\bar{3}3$	147	- 128	150	- 136
$\bar{6}33$	- 115	- 74	62	- 90
$\bar{7}33$	164	157	194	178
034	390	362	371	357
$\bar{1}34$	310	- 335	336	- 335
$1\bar{3}4$	135	152	141	150
$\bar{2}34$	140	- 114	132	- 115
$2\bar{3}4$	494	- 506	539	- 490
$\bar{3}34$	240	257	265	275
$3\bar{3}4$	116	127	132	131
$\bar{4}34$			- 26	- 47
$4\bar{3}4$	346	339	353	342
$\bar{5}34$			88	- 132
$5\bar{3}4$	236	- 269	274	- 276
$\bar{6}34$	161	- 110	141	- 119
$\bar{7}34$	179	189	230	209
035	264	- 253	238	- 245
$\bar{1}35$	190	177	194	187
$1\bar{3}5$	- 70	- 9	- 35	- 6
$\bar{2}35$	146	143	168	155
$2\bar{3}5$	348	339	362	338
$\bar{3}35$	144	- 109	150	- 117
$3\bar{3}5$	165	- 156	185	- 148
$\bar{4}35$	221	- 225	221	- 232
$\bar{5}35$	168	183	185	176
$\bar{6}35$	- 108	18	- 26	21

hkl	F_o	F_c	F_o	F_c
$\bar{7}35$	154	- 150	168	- 162
036	288	- 273	274	- 258
136	- 99	80	71	81
$\bar{1}36$	- 74	54	44	52
236	124	126	150	127
$\bar{2}36$	313	293	344	275
336			79	- 112
$\bar{3}36$	234	- 226	247	- 211
436	185	- 163	212	- 156
$\bar{4}36$	244	245	247	236
636	- 102	- 5		
$\bar{7}36$	137	- 148		
037	153	158		
$\bar{1}37$	- 142	- 106		
$\bar{2}37$	281	- 216		
337	- 141	116		
$\bar{4}37$	- 141	48		
$\bar{5}37$	168	- 177		
038	74	126		
$\bar{1}38$	67	- 95		
$\bar{2}38$	- 148	- 111		
$\bar{3}38$	217	162		
040	955	- 911	1015	- 940
140	180	180	194	173
240	433	430	406	438
340	660	- 648	618	- 686
440	192	- 208	230	- 227
540	377	376	477	416
640	- 136	- 73	106	- 90
740	203	- 183	221	- 223
041	202	- 188	230	- 202
141	- 77	103	97	95
$\bar{1}41$	- 66	43	- 26	38
241	238	227	238	232
$\bar{2}41$	244	237	291	251
341	- 89	- 46	- 35	- 43
$\bar{3}41$	105	97	124	118
441	130	- 102	141	- 110
$\bar{4}41$			- 71	84
541			- 71	5
$\bar{5}41$			97	83
641			- 71	1
$\bar{6}41$			- 71	8
$\bar{7}41$			- 35	27
042	497	495	547	491
142	- 78	- 26	26	- 39

hkl	F_o	F_c	F_o	F_c
$\bar{1}42$	657	- 651	724	- 661
$2\bar{4}2$	640	- 623	636	- 656
$\bar{2}42$	303	- 321	353	- 331
$3\bar{4}2$	176	192	212	202
$\bar{3}42$	611	643	636	649
$4\bar{4}2$	231	226	256	248
$\bar{4}42$	138	- 155	177	- 172
$5\bar{4}2$	266	- 271	362	- 311
$\bar{5}42$	430	- 465	512	- 501
$6\bar{4}2$			71	- 83
$\bar{6}42$	196	199	247	227
$\bar{7}42$	96	144	168	164
043	212	208	221	215
$1\bar{4}3$	- 86	37	79	40
$\bar{1}43$	183	190	247	202
$2\bar{4}3$	- 97	- 37	- 35	- 45
$\bar{2}43$	177	188	221	200
$3\bar{4}3$	- 109	106	62	98
$\bar{3}43$	147	155	177	162
$4\bar{4}3$	122	104	124	105
$\bar{4}43$			62	25
$5\bar{4}3$			- 35	- 18
$\bar{5}43$			- 35	68
$6\bar{4}3$			141	164
$\bar{7}43$			106	70
044	287	- 293	318	- 230
$1\bar{4}4$	266	- 273	265	- 274
$\bar{1}44$	478	495	539	473
$2\bar{4}4$	316	315	327	324
$\bar{2}44$	133	- 86	106	- 97
$3\bar{4}4$	- 114	- 35	35	- 42
$\bar{3}44$	523	- 547	583	- 540
$4\bar{4}4$	207	- 228	274	- 255
$\bar{4}44$	296	315	318	323
$5\bar{4}4$	277	282	291	287
$\bar{5}44$	291	- 306	353	- 329
$\bar{7}44$	- 127	- 49		
$\bar{8}44$	157	160		
045	133	118	150	121
$1\bar{4}5$			71	89
$\bar{1}45$	143	137	159	140
$2\bar{4}5$			71	88
$\bar{2}45$	- 76	27	26	35
$3\bar{4}5$			- 26	19
$\bar{3}45$	- 79	48	62	64
$4\bar{4}5$	166	187	194	206
$\bar{5}45$	150	104	177	124
$\bar{6}45$			- 35	- 17
$\bar{7}45$			- 26	19

hkl	F_o	F_c	F_o	F_c
046	- 92	29	- 26	26
146	204	210	212	199
$\bar{1}46$	310	- 315	318	- 292
246	128	- 137	168	- 143
$\bar{2}46$	214	206	238	199
$\bar{3}46$	252	269	212	250
$\bar{4}46$	304	- 318	362	- 306
$\bar{5}46$	- 95	- 61	44	- 51
$\bar{6}46$	303	278	327	286
$\bar{1}48$	248	228		
150	355	348	397	370
250	262	- 229	283	- 236
350	- 113	- 122	79	- 131
450	334	310	388	346
550			- 44	49
650			168	- 149
750			79	69
051	418	- 383	459	- 397
151	512	488	574	507
$\bar{1}51$	787	- 738	909	- 764
251	196	- 225	238	- 244
$\bar{2}51$	375	394	424	417
351	448	- 403	450	- 437
$\bar{3}51$	213	191	221	208
451	169	180	194	211
$\bar{4}51$	451	- 478	530	- 524
551	- 113	23	62	37
$\bar{5}51$	- 105	- 31	44	- 41
651	181	- 179	212	- 219
$\bar{6}51$	179	174	230	207
751			88	- 109
052	103	122	124	126
152	378	- 372	406	- 390
$\bar{1}52$	116	132	132	135
252	- 91	- 9	- 35	- 9
$\bar{2}52$	504	- 506	627	- 536
352	153	166	150	187
$\bar{3}52$	120	- 150	141	- 176
452	165	- 144	221	- 158
$\bar{4}52$	209	239	238	243
552			- 26	- 72
$\bar{5}52$	169	- 142	238	- 162
652			115	118
$\bar{6}52$	153	- 190	212	- 221
752			79	60
053	415	402	450	411
153	506	- 499	477	- 518

hkl	F_o	F_c	F_o	F_c
$\bar{1}53$	315	318	362	325
$\bar{2}53$	204	- 207	221	- 214
$\bar{2}53$	653	- 651	697	- 674
$\bar{3}53$	215	219	256	242
$\bar{3}53$	152	- 148	203	- 168
$\bar{4}53$			71	- 95
$\bar{4}53$	370	374	380	393
$\bar{5}53$			141	- 126
$\bar{5}53$			97	- 117
$\bar{6}53$			159	- 153
$\bar{7}53$			132	135
054	324	- 342	362	- 356
$\bar{1}54$	121	103	124	105
$\bar{1}54$	199	- 201	256	- 219
$\bar{2}54$	- 107	19	- 26	21
$\bar{2}54$	187	207	212	193
$\bar{3}54$	192	- 184	212	- 198
$\bar{3}54$	192	- 176	238	- 188
$\bar{4}54$			- 35	- 1
$\bar{4}54$	292	- 306	300	- 329
$\bar{5}54$	- 107	86	79	70
$\bar{6}54$	- 117	26	- 35	12
$\bar{7}54$	155	- 139	159	- 163
055	391	- 377	397	- 384
$\bar{1}55$	169	186	177	186
$\bar{1}55$	103	- 112	132	- 121
$\bar{2}55$	182	169	203	175
$\bar{2}55$	411	394	450	390
$\bar{3}55$	171	- 166	177	- 179
$\bar{3}55$	- 88	- 74	53	- 59
$\bar{4}55$	220	209	238	- 208
$\bar{5}55$	158	182	185	175
$\bar{6}55$			- 26	25
$\bar{7}55$			132	- 124
056	120	100	71	91
$\bar{1}56$	141	- 110	132	- 115
$\bar{1}56$	- 90	- 83	79	- 89
$\bar{2}56$			88	122
$\bar{2}56$	238	- 227	274	- 231
$\bar{3}56$	- 87	70	53	48
$\bar{4}56$	- 92	33	- 26	14
$\bar{5}56$	191	- 187	212	- 197
060	290	265	371	305
$\bar{1}60$	271	293	336	323
$\bar{2}60$	158	137	194	150
$\bar{3}60$	- 110	- 38	- 26	- 34
$\bar{4}60$	- 119	116	62	133
$\bar{5}60$	175	189	221	217

hkl	F_o	F_c	F_o	F_c
660			79	28
061	797	766	874	798
161	- 84	- 36	35	- 39
161	271	- 291	318	- 302
261	622	- 603	671	- 639
261	507	- 502	530	- 521
361	231	232	256	258
361	381	395	433	430
461	231	243	247	269
461	- 100	86	71	89
561	200	- 200	256	- 240
561	286	- 276	344	- 318
661			- 26	- 19
661			150	114
062	137	148	177	157
162	189	165	221	181
162	- 84	- 6	- 35	9
262	127	110	124	132
262	125	161	177	187
362			150	189
362	255	292	318	320
462			124	92
462			88	33
562			- 35	- 26
562			124	- 89
063	433	- 439	459	- 449
163	161	- 176	194	- 179
163	401	407	450	419
263	402	411	415	443
263	139	144	159	146
363	- 118	- 55	79	- 61
363	451	- 456	494	- 472
463	202	- 224	247	- 254
463	116	125	141	142
563			115	120
563	234	241	274	268
663	208	- 210	247	- 239
763			88	- 74
064	- 96	24	44	38
164			- 35	15
164	148	156	177	163
264			71	103
264			- 35	19
364			71	42
364			97	- 83
464			- 35	5
464			44	73
364			106	63

hkl	F_o	F_c	F_o	F_c
$\bar{6}64$			- 35	- 63
065	142	103	106	107
165	205	206	212	213
$\bar{1}65$	376	- 369	406	- 363
265	189	- 186	203	- 197
$\bar{2}65$	110	83	97	88
365			35	- 52
$\bar{3}65$	324	312	353	314
465	257	- 250	256	- 255
$\bar{4}65$	144	139	141	- 147
565	236	215	221	230
066			- 26	14
166			- 26	33
$\bar{1}66$			- 44	- 43
$\bar{2}66$			- 26	13
$\bar{3}66$			- 26	- 5
$\bar{4}66$			17	- 93
$\bar{5}66$			- 26	- 24
170	522	511	600	555
270	232	- 252	265	- 269
370	312	- 294	318	- 331
470	200	224	247	242
570	- 136	7	- 35	1
670	171	- 157	212	- 193
071	- 89	3	- 35	- 11
171	236	- 235	283	- 263
$\bar{1}71$	- 89	80	35	70
271	113	67	97	66
$\bar{2}71$	305	- 291	371	- 325
371	- 103	65	- 44	66
$\bar{3}71$	- 97	- 80	- 44	- 95
471	197	- 190	247	- 223
$\bar{4}71$	205	203	238	220
571			- 44	- 55
$\bar{5}71$			124	- 69
671			97	106
$\bar{6}71$			159	- 162
072	214	211	265	224
172	348	- 385	441	- 419
$\bar{1}72$	390	415	494	451
272	- 110	116	71	120
$\bar{2}72$	202	- 238	256	- 234
372	332	319	380	355
$\bar{3}72$	- 99	25	- 35	37
472			132	- 159
$\bar{4}72$	346	359	397	398
572			132	- 125

hkl	F_o	F_c	F_o	F_c
$\bar{3}72$			44	- 76
$\bar{6}72$			141	- 114
073	161	- 177	185	190
$\bar{1}73$	134	111	132	109
$\bar{1}73$	115	- 104	150	- 113
$\bar{2}73$	- 115	- 27	71	- 39
$\bar{2}73$	213	215	256	216
$\bar{3}73$	168	- 135	159	- 157
$\bar{3}73$	- 104	- 66	106	- 80
$\bar{4}73$			88	52
$\bar{4}73$	179	- 213	230	- 232
$\bar{5}73$			168	105
$\bar{6}73$			62	96
773			88	- 94
074	150	- 131	132	- 126
$\bar{1}74$	267	277	300	299
$\bar{1}74$	- 100	20	- 35	30
$\bar{2}74$	- 119	88	106	97
274	405	400	459	420
$\bar{3}74$	180	- 154	185	- 175
$\bar{3}74$	- 103	- 60	- 26	- 51
$\bar{4}74$	166	- 170	168	- 162
$\bar{5}74$	244	271	300	309
$\bar{6}74$	159	124	177	149
075	128	116	115	111
$\bar{1}75$	139	- 80	97	- 86
$\bar{1}75$	- 104	- 5	- 26	- 10
275			- 26	- 56
$\bar{2}75$	139	- 152	168	- 151
$\bar{3}75$	- 104	100	141	106
$\bar{4}75$	- 110	104	97	104
$\bar{5}75$	135	- 120	132	- 129
076	205	218	194	224
$\bar{1}76$			- 26	- 6
$\bar{1}76$			- 26	- 5
$\bar{2}76$	152	- 148	150	- 133
$\bar{3}76$	229	230	247	243
$\bar{4}76$	169	155	194	170
$\bar{5}76$	178	- 165	159	- 157
080	372	381	503	411
180	203	- 215	283	- 242
280	416	- 407	450	- 455
380	219	217	265	250
480	- 130	67	62	81
580	229	- 233	291	- 285
081	136	145	159	148

hkl	F_o	F_c	F_o	F_c
181	- 97	- 12	- 44	- 17
$\bar{1}81$	- 104	- 106	132	- 119
281	142	- 141	177	- 151
$\bar{2}81$	166	- 162	212	- 179
381			- 44	81
$\bar{3}81$			- 44	43
481			88	69
$\bar{4}81$			- 44	- 17
581			- 44	- 39
$\bar{5}81$			141	- 107
681			53	- 9
082	442	- 451	539	- 494
182	167	- 196	212	- 219
$\bar{1}82$	287	307	371	335
282	261	262	300	291
$\bar{2}82$	165	191	238	210
382	- 118	- 108	124	- 128
$\bar{3}82$	433	- 430	486	- 484
482	160	- 162	185	- 195
$\bar{4}82$	- 113	- 49	- 35	- 65
582			88	112
$\bar{5}82$	182	209	256	244
682			132	- 104
083	143	- 164	168	- 181
183	147	- 103	150	- 112
$\bar{1}83$	- 107	41	44	27
283			- 35	62
$\bar{2}83$	- 107	- 11	- 35	- 31
383			- 26	- 27
$\bar{3}83$	159	- 162	194	- 189
483			88	- 70
$\bar{4}83$			106	- 56
583			- 26	1
$\bar{5}83$			62	- 86
084	180	187	212	199
184	183	199	212	217
$\bar{1}84$	384	- 381	433	- 413
284	219	- 224	265	- 250
$\bar{2}84$	- 109	- 86	106	- 105
384			44	- 80
$\bar{3}84$	297	308	353	329
484	- 116	- 87	97	- 83
$\bar{4}84$	160	- 140	177	- 153
584			141	134
085	- 117	- 12	- 35	- 24
185			- 35	13
$\bar{1}85$	157	- 140	168	- 155
285			44	- 81

hkl	F_o	F_c	F_o	F_c
$\bar{2}85$			62	- 61
$\bar{3}85$			- 35	11
$\bar{4}85$			62	- 98
$\bar{5}85$			97	- 75
086	- 118	- 48		
186	175	- 160		
$\bar{1}86$	217	219		
$\bar{2}86$	- 111	- 47	- 71	- 39
$\bar{3}86$	152	- 146	141	- 148
$\bar{4}86$	139	143	132	138
190	213	- 238	283	- 267
290			79	62
390			97	147
490			62	- 69
590			- 26	- 21
091	171	186	247	224
$\bar{1}91$	175	- 178	212	- 172
$\bar{1}91$	347	336	424	382
$\bar{2}91$	178	204	221	248
$\bar{2}91$	165	- 184	185	- 194
$\bar{3}91$	252	227	283	269
$\bar{3}91$	- 110	- 22	- 44	- 9
$\bar{4}91$			141	- 150
$\bar{4}91$	307	307	380	368
$\bar{5}91$			- 35	2
092	- 108	- 54	- 35	- 55
192	190	186	230	212
$\bar{1}92$	153	- 167	194	- 180
$\bar{2}92$	- 116	- 17	44	- 20
$\bar{2}92$			115	91
$\bar{3}92$	123	- 130	141	- 151
$\bar{3}92$			- 26	41
$\bar{4}92$			71	44
$\bar{4}92$			62	- 95
$\bar{5}92$			79	41
093	139	- 132	132	- 130
$\bar{1}93$	250	257	274	292
$\bar{1}93$	- 115	- 76	88	- 66
$\bar{2}93$			79	79
$\bar{2}93$	333	334	371	376
$\bar{3}93$			132	- 125
$\bar{3}93$	- 120	2	- 35	9
$\bar{4}93$	200	- 214	230	- 235
$\bar{5}93$			150	148
$\bar{6}93$			115	127
094	- 119	68	62	75

hkl	F_o	F_c	F_o	F_c
$\bar{1}94$			115	- 100
$\bar{1}94$	- 116	30	- 35	31
$2\bar{9}4$			- 35	- 25
$\bar{2}94$	139	- 115	124	- 121
$\bar{3}94$			62	37
$\bar{4}94$			62	80
$\bar{5}94$			115	- 89
095	184	173	168	187
$1\bar{9}5$			71	- 85
$\bar{1}95$	- 121	15	- 35	19
$\bar{2}95$	194	- 196	212	- 200
$\bar{3}95$			97	111
$\bar{4}95$			132	122
$\bar{5}95$			150	- 173
hk l				
0100	162	152	177	166
1100	- 126	- 47	- 44	- 63
2100	186	- 160	194	- 199
3100			- 44	9
4100			53	37
5100			- 35	- 47
0101	276	- 268	318	- 312
1101	- 112	42	- 44	49
$\bar{1}101$	157	156	185	179
2101	257	245	274	291
$\bar{2}101$	184	209	230	252
3101	132	- 127	150	- 150
$\bar{3}101$	175	- 169	185	- 185
4101			79	- 135
$\bar{4}101$			- 44	11
$\bar{5}101$			177	203
0102	147	- 159	185	- 194
$1\bar{1}02$			62	- 57
$\bar{1}102$			- 35	28
$2\bar{1}02$			106	109
$\bar{2}102$			79	68
$3\bar{1}02$			- 35	- 37
$\bar{3}102$			79	- 90
$4\bar{1}02$			62	- 89
$\bar{4}102$			71	- 26
0103	222	209	247	246
1103	- 129	91	115	107
$\bar{1}103$	- 134	- 132	141	- 133
2103	157	- 154	177	- 183
$\bar{2}103$	- 123	10	- 35	22
3103			62	70

hk l	F_o	F_c	F_o	F_c
$\bar{3}103$	252	251	256	292
$\bar{4}103$			44	- 45
$\bar{5}103$			79	- 101
0104			- 26	49
1104			44	34
$\bar{1}104$			79	- 93
2104			53	- 82
$\bar{2}104$			- 26	- 24
3104			62	69
$\bar{4}104$			- 26	- 36
$\bar{5}104$			26	- 37
0105	- 131	- 5	- 35	2
$\bar{1}105$	198	192	177	216
$\bar{2}105$	- 128	- 22	- 35	- 15
$\bar{3}105$	- 130	- 108	88	- 104
$\bar{4}105$	187	162	177	194
1110	217	- 224	256	- 259
2110	- 139	118	115	149
3110	150	128	177	159
4110			115	- 143
0111			79	- 101
1111			- 44	45
$\bar{1}111$			124	- 144
2111			71	- 60
$\bar{2}111$			35	55
3111			53	- 86
$\bar{3}111$			- 35	18
$\bar{4}111$			115	- 114
0112	170	- 135	168	- 163
1112	180	182	185	208
$\bar{1}112$	190	- 196	230	- 234
2112			- 44	- 23
$\bar{2}112$	180	161	185	179
3112			106	- 163
$\bar{3}112$	- 128	30	- 35	24
$\bar{4}112$	190	- 176	194	- 225
0113			71	72
1113			106	- 104
$\bar{1}113$			44	48
$\bar{2}113$			124	- 141
$\bar{3}113$			- 26	- 56
$\bar{4}113$			35	67
0114	142	115	115	122
$\bar{1}114$	- 132	38	- 35	31
$\bar{2}114$	204	- 204	230	- 245

hk l	F_o	F_c	F_o	F_c
0120	- 143	- 111	115	- 113
1120	- 143	98	115	137
2120	184	154	177	199
3120			88	- 91
0121			35	- 50
$\bar{1}121$			35	69
$\bar{2}121$			- 44	26
0122	177	162	168	204
$\bar{1}122$			44	77
$\bar{1}122$	- 130	- 78	53	- 81
$\bar{2}122$			53	- 94
$\bar{2}122$	- 132	- 31	- 35	- 22
$\bar{3}122$	169	164	150	212
0123			- 26	38
$\bar{1}123$			35	- 97
$\bar{1}131$	175	147		
$\bar{1}131$	183	- 153		

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